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STATISTICAL PHYSICS

Introduction

Statistical mechanics is the science of predicting the observable properties of a many body system by studying the statistics of the behaviour of its individual constituents like atoms, molecules, photons, electrons, phonons, quarks etc. Thus with the help of statistical mechanics we are able to explain the following:

1. Thermionic emission
2. Photoelectric effect
3. Black body radiation
4. Stellar properties
5. All stars, neutron stars, white dwarfs etc.
6. Thermal and electric properties of solids. (Thermal conductivity, specific heat of solids, electrical conductivity etc.)
7. Magnetic properties of materials. (Dia, Para, ferro, susceptibility etc.)

The very name statistical mechanics implies that it is not concerned with the actual motions or interactions of individual particle but instead with what is most likely to happen. It never tells us the history of one of the particles of the system but it tells us the probability that the particle has a certain amount of energy at a certain moment. Statistical mechanics can be applied to classical systems (molecules in a gas) as well as to quantum mechanical systems (electrons, photons etc.)

Statistical analysis

In physics many of the experiments are analysed as if the interactions takes place in single, isolated events. For example in Rutherford scattering and Compton scattering experiments treated the events as single and isolated. Suppose we consider another simple experiment that we supply heat energy to a gas constituting large number of particles (atoms). The energy that we supply will go to all the particles. Here the system cannot be treated as a single entity (or event). At the same time we cannot analyse the behaviour of individual atoms which are millions of millions in number. Such systems could be analysed by the technique of statistical mechanics. That is statistical mechanics deals with the collective behaviour of the system. In this analysis we are not concerned with or not possible to have the exact outcome of single particle. But statistical mechanics predicts the average outcome of the collec-

tive behaviour of particles or events based on the statistical distribution of all the possible outcomes. The above discussion shows that whenever a system containing large number of particles the concept of statistical mechanics is necessary.

Apart from the simple experiment quoted above there are so many complex systems that contain large number of particles such as the spectrum given out by mercury vapour while passing electric current through it and the thermionic emission of tungsten filament of an ordinary incandescent light bulb etc. In the case of spectrum millions of photons take part in the process and in the case of thermionic emission millions of electrons take part. How do we analyse such complex systems which contain infinitely large number of particles. Statistical analysis provides the exact prediction of the output. Here we discuss how statistical analysis is done.

It may seem that there are two possible ways to approach the analysis of a complex system. First is to specify a set of microscopic properties such as position and velocity of each atom. Even for a pinch of matter contains very large number of particles (Avogadro number 6.02×10^{23} per mole). Assigning positions and velocities to 10^{23} atoms and then to proceed is an impossible task. The second approach is understanding and predicting the behaviour of systems containing many particles in terms of a few macroscopic properties such as the pressure, temperature etc. The development of relationship between microscopic and macroscopic properties was one of greatest achievements, which plays a crucial role in the development of statistical mechanics.

Macroscopic property of a system

It is the behaviour exhibited by the system at macroscopic level. Pressure, temperature, energy are some of the macroscopic properties of gas. These properties are observable and can be measured.

Microscopic property of a system

It is the behaviour exhibited by individual constituents of the system or it is the behaviour of the system at microscopic level.

Macrostate and microstate

Consider the macroscopic property energy (E) of the system. This energy is due to the contributions coming from individual particles. Thus the energy (E) of the system can be achieved in different possible ways of energy distributions of individual particles. Each possible arrangement is called the macrostate of the system. In each macrostate a number of different arrangements of particles is possible to get the same energy E. Each different arrangement is known as the microstate of the system. This can be clarified by taking examples.

Consider the distribution of 2 units of energy to a system (gas) containing four identical but distinguishable particles A, B, C and D. Assume that each particle can acquire energy only in integral units.

	Energy of the particle				Total energy
Macrostate I	A	B	C	D	
	2	0	0	0	2
Macrostate II	1	1	0	0	2

Thus our system has only two macrostates.

But in macrostate we can distribute energy among particles in different ways.

	Energy of the particle				Total energy
Macrostate I	A	B	C	D	
	2	0	0	0	2
	0	2	0	0	2
	0	0	2	0	2
	0	0	0	2	2

Thus we have 4 possible arrangements in macrostate I. That is Macrostate I has four possible microstates.

	Energy of the particle				Total energy
Macrostate II	A	B	C	D	
	1	1	0	0	2
	1	0	1	0	2
	1	0	0	1	2
	0	1	1	0	2
	0	0	1	1	2
	0	1	0	1	2

Here we have 6 possible arrangements in the macrostate II. That is macrostate II has 6 microstates.

The number of microstates in a given macrostate is called multiplicity denoted by W. In our system

$$W_1 = 4 \text{ and } W_2 = 6.$$

By counting the number of microstates we can make a statistical analysis.

One application of the counting of multiplicity is to determine the direction of the natural evolution of the system. According to second law of thermodynamics an

isolated systems evolve in a direction of increasing entropy, our system evolves along the direction of multiplicity. Thus we can say that when multiplicity increases entropy of the system also increases. That is, if we started our system in the microstate I and allowed the particles to interact with one another, after sometime the system would be in the macrostate II. If the system is in the macrostate II after sometime, the system is less likely to find in macrostate I. This is because multiplicity decreases in going from macrostate II to I as the natural system evolves along the direction of multiplicity.

In the above statistical analysis there is an implicit postulate.

That is "all microstates are equally probable".

In our system considered there are totally 10 ($4 + 6$) microstates. According to the postulate our system can be found with equal probability in any of the 10 microstates. Since there are 6 microstates in macrostate II and 4 microstates in macrostate I, the system is more likely to be found in macrostate II. This probability is obviously

$\frac{6}{10} = 60\%$. Thus the probability of finding the system in the macrostate I is

$\frac{4}{10} = 40\%$. i.e., The system is found in the macrostate I with 40% probability and in macrostate II with 60% probability.

This shows that the above said postulate enables us to calculate the probability of occurrence of the system in different macrostates. (see examples 1 and 2).

We can conclude this section by saying that the statistical analysis of a complex system gives us a way of describing the system, its average properties and its evolution in time.

Example 1

- Considering the numbers of heads and tails, how many macrostates are there when 4 coins are tossed.
- What is the total number of possible microstates in tossing 4 coins.
- Find the total number of microstates for each macrostate.

Solution

- When 4 coins are tossed there are 5 different distributions. They are (0H, 4T), (1H, 3T), (2H, 2T), (3H, 1T) and (4H, 0T) so we have five macrostates.
- To find the total number microstates, we have to find out all possible distributions in each macrostate. See the table below.

	Macrostate		Microstate	Number of microstates W
	Head (\uparrow) Tail (\downarrow)			
1)	0	4	$\downarrow\downarrow\downarrow\downarrow$	1
2)	1	3	$\uparrow\downarrow\downarrow\downarrow$ $\downarrow\uparrow\downarrow\downarrow$ $\downarrow\downarrow\uparrow\downarrow$ $\downarrow\downarrow\downarrow\uparrow$	4
3)	2	2	$\uparrow\uparrow\downarrow\downarrow$ $\uparrow\downarrow\uparrow\downarrow$ $\downarrow\uparrow\downarrow\uparrow$ $\downarrow\uparrow\uparrow\downarrow$ $\downarrow\downarrow\uparrow\uparrow$ $\uparrow\downarrow\downarrow\uparrow$	6
4)	3	1	$\uparrow\uparrow\uparrow\downarrow$ $\uparrow\uparrow\downarrow\uparrow$ $\uparrow\downarrow\uparrow\downarrow$ $\downarrow\uparrow\uparrow\uparrow$	4
5)	4	0	$\uparrow\uparrow\uparrow\uparrow$	1

∴ Total number of microstates = $1 + 4 + 6 + 4 + 1 = 16$

or Each toss has 2 possible outcomes, so
the total number of possible outcomes = $2^4 = 16$

Example 2

A collection of three non-interacting particles shares 3 units of energy. Each particle is restricted to having an integral number of units of energy.

- (a) How many macrostates are there?
- (b) How many microstates are there in each of the macrostates
- (c) What is the probability of finding one of the particles with 2 units of energy?
With 0 units of energy?

Solution

		A	B	C	Total energy
a)	Macrostates 1	3	0	0	3
	Macrostate 2	2	1	0	3
	Macrostate 3	1	1	1	3

Thus there are 3 macrostates.

- b) In macrostate 1, there are 3 different ways of arrangements

A	B	C
3	0	0
0	3	0
0	0	3

In macrostate 2

A	B	C
2	1	0
2	0	1
1	2	0
1	0	2
0	1	2
0	2	1

So there are 6 microstates.

In macrostate 3	A	B	C
	1	1	1

There is only one possible arrangement, so there is only one microstate.

- c) There are totally $3 + 6 + 1 = 10$ microstates.

The probability of occurrence of 2 units of energy in macrostate 1 is zero, because none of the particles in macrostate 1 has 2 units of energy.

In macrostate 2, there are 6 microstates.

∴ Probability of the macrostate 2

$$= \frac{6}{10} = 60\%.$$

Only one of the particles in macrostate 2 has 2 units of energy.

∴ Probability of finding one of the particles with energy 2 units

$$= \frac{1}{3} \times \frac{6}{10} = 0.2 = 20\%.$$

None of the particles has 2 unit of energy in the macrostate 3.

$$\therefore \text{Overall probability} = \frac{0}{3} \times \frac{3}{10} + \frac{1}{3} \times \frac{6}{10} + \frac{0}{3} \times \frac{1}{10} = 20\%.$$

0 units of energy probability

The probability of finding one of the particles in the macrostate 1

$$= \frac{2}{3} \times 30\% = 20\%.$$

$$\text{In macrostate 2} = \frac{1}{3} \times 60\% = 20\%$$

In macrostate 3 none of the particles has 0 unit of energy, so probability = 0

$$\therefore \text{Overall probability} = 40\%.$$

Generalisation of probability

We have from (c) of the example 2

$$P(\varepsilon = 2) = \frac{0}{3} \times \frac{3}{10} + \frac{1}{3} \times \frac{6}{10} + \frac{0}{3} \times \frac{1}{10}$$

Generalising this result, we get

$$P(\varepsilon) = \frac{N_1}{N} \frac{W_1}{W_{\text{total}}} + \frac{N_2}{N} \frac{W_2}{W_{\text{total}}} + \frac{N_3}{N} \frac{W_3}{W_{\text{total}}}$$

Where N_1 is the number of particles with energy ε , in the first macrostate 1 with multiplicity W_1 and W_{total} is the overall total multiplicity.

N_2 is the number of particles with energy ε , in the macrostate 2 with multiply W_2 . Similarly W_3 is the number of particles with energy ε in the macrostate 3 with multiplicity W_3 . In general we can write.

$$P(\varepsilon) = \frac{\sum_i N_i W_i}{N \sum_i W_i} \quad \dots \dots (1)$$

where i runs over all the macrostates.

Classical and quantum statistics

In classical statistics particles are identical but distinguishable whereas in quantum statistics particles are treated as identical but indistinguishable. It is due to this difference the multiplicity and the probability will be different in the two regimes. By taking a simple example we can illustrate this.

Classical

Consider the distribution of 6 units of energy to a system containing only 5 identical but distinguishable particles. Assume that these particles can acquire energy only in integral units and also acquire 0 unit of energy.

Here there are 10 macrostates (see tabular column below)

Energy of the particles (Table I)

Macrostates	0	1	2	3	4	5	6	Total energy
1	4	0	0	0	0	0	1	6
2	3	1	0	0	0	1	0	6
3	3	0	1	0	1	0	0	6
4	2	2	0	0	1	0	0	6
5	2	1	1	1	0	0	0	6
6	3	0	0	2	0	0	0	6
7	2	0	3	0	0	0	0	6
8	1	3	0	1	0	0	0	6
9	1	2	2	0	0	0	0	6
10	0	4	1	0	0	0	0	6

We obtained 10 macrostates. The multiplicity of each microstate in the macrostate can be calculated as before. That method of finding the number of microstates by drawing tabulator column is laborious and time consuming. So to evaluate the number of microstate (multiplicity W) we introduce a formula

$$W = \frac{N!}{N_0! N_1! N_2! N_3! N_4! N_5! N_6!} \quad \dots \dots (2)$$

Where N is the total number of particles and $N_0, N_1, N_2, N_3, N_4, N_5, N_6$ are the number of particles with energies 0, 1, 2, 3, 4, 5, and 6 respectively. In general

$$W = \frac{N!}{\prod_{i=0}^6 N_i!} \quad \dots \dots (3)$$

Remember that

$$N_0 + N_1 + N_2 + N_3 + N_4 + N_5 + N_6 = N$$

and $0 \times N_0 + 1 \times N_1 + 2 \times N_2 + 3N_3 + 4N_4 + 5N_5 + 6N_6 = \text{Total energy}$

For example, in the macrostate 1

$$N_0 = 4, N_1 = 0, N_2 = 0, N_3 = 0, N_4 = 0, N_5 = 0 \text{ and } N_6 = 1$$

$$\therefore N = 5$$

$$W_1 = \frac{5!}{4! 1!} = \frac{1.2.3.4.5}{1.2.3.4} = 5$$

Similarly we can calculate all multiplicities

$$W_2 = 20$$

$$W_3 = 20$$

$$W_4 = 30$$

$$W_5 = 60$$

$$W_6 = 10$$

$$W_7 = 10$$

$$W_8 = 20$$

$$W_9 = 30$$

$$W_{10} = 5$$

\therefore The overall total number of microstates

$$W_{\text{total}} = 5 + 20 + 20 + 30 + 60 + 10 + 10 + 20 + 30 + 5$$

$$W_{\text{total}} = 210.$$

When there are N particles share Q integral units of energy.

$$W_{\text{total}} = \frac{(N+Q-1)!}{Q!(N-1)!} \quad \dots \dots (4)$$

In our problem $N = 5, Q = 6$

$$\therefore W_{\text{total}} = \frac{(5+6-1)}{6! 4!} = \frac{10!}{6! 4!} = 210.$$

We already calculated the general expression for the probability of finding one of particles with energy ε .

$$\text{i.e., } P(\varepsilon) = \frac{\sum N_i W_i}{N \sum W_i} \quad \dots \dots (5)$$

i runs over all macrostates. ($i = 1$ to 10)

$$P(0) = \frac{5 \times 5 + 4 \times 20 + 4 \times 20 + 4 \times 30 + 3 \times 60 + 5 \times 10 + 5 \times 10 + 4 \times 20 + 4 \times 30 + 5 \times 5}{10 \times 210}$$

$$P(0) = \frac{25 + 80 + 80 + 120 + 180 + 50 + 50 + 80 + 120 + 25}{2100}$$

$$P(0) = 0.4 \text{ similarly, we get}$$

$$P(1) = 0.267 \quad P(5) = 0.019$$

$$P(2) = 0.167 \quad P(6) = 0.005$$

$$P(3) = 0.095$$

$$P(4) = 0.048$$

Summing all the probabilities over all energy states we get unity.

$$\text{i.e., } \sum_{i=0}^6 P(\varepsilon_i) = 1$$

When we draw a graph between energy along the x-axis and probability $P(\varepsilon)$ along the y-axis, we get a graph as shown in figure below.

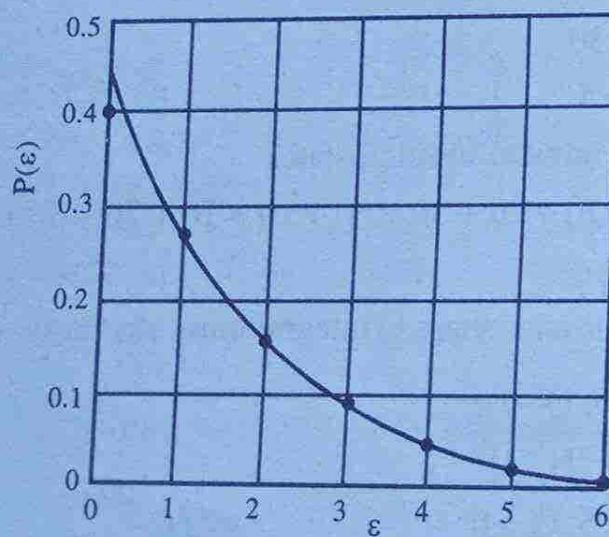


Figure 1.1: Probability graph
(The curve is an exponential function that closely fits the points)

The smooth curve obtained is an exponentially decreasing curve.

$$\text{i.e., } P(\varepsilon) \propto e^{-\beta\varepsilon}$$

Where β is a constant to be chosen to fit the curve.

The whole discussion shows that for classical particle the probability distribution is an exponential function.

$$\text{Note : } P(\varepsilon_i) = A^{-1} e^{-\beta\varepsilon_i}$$

Summing over all energy states, we get

$$\sum P(\varepsilon_i) = A^{-1} \sum_{i=1} e^{-\beta\varepsilon_i}$$

But

$$\sum_i P(\varepsilon_i) = 1$$

$$\therefore 1 = A^{-1} \sum_{i=1} e^{-\beta\varepsilon_i}$$

or

$$A^{-1} = \frac{1}{\sum_{i=1} e^{-\beta\varepsilon_i}}$$

$$\therefore P(\varepsilon_i) = \frac{e^{-\beta\varepsilon_i}}{\sum_{i=1} e^{-\beta\varepsilon_i}} \quad \dots\dots (6)$$

Quantum statistics

In quantum mechanics particles are treated as identical and indistinguishable. So while enumerating the multiplicity in quantum statistics it will be different from that of classical statistics. For example consider a macrostate in classical statistics. The classical system containing three distinguishable particles A, B and C with energies 2, 1 and 3 units respectively with total energy 6 units. Here we consider only one macrostate.

$$\text{i.e., Macrostate is} \quad \begin{array}{ccc} A & B & C \\ 2 & 1 & 3 \end{array}$$

These energies 2, 1 and 3 can be distributed to the particles A, B and C in different ways. The number of different arrangements gives the number of microstates (multiplicity)

i.e.,

A	B	C
2	1	3
1	2	3
2	3	1
1	3	2
3	1	2
3	2	1

6 numbers

Thus the number of microstates (multiplicity) in the particular macrostate is 6.

In quantum statistics particles are indistinguishable. So $A = B = C \equiv A$

\therefore The corresponding macrostate in quantum statistics for the above example is

$$\begin{array}{ccc} A & A & A \\ 2 & 1 & 3 \end{array}$$

Here no more different arrangements of distributing energies to particles is possible. Hence the number of microstate (multiplicity) is one.

If you take any other macrostate, the corresponding number of state is always one. Thus, we can say that for identical indistinguishable (quantum) particles the multiplicity of each macrostate is always one.

Another important restriction imposed by quantum particles is the accommodation of number particles in each state. For example suppose we deal with electrons

$\left(\text{spin } \frac{1}{2}\right)$. According to Pauli's exclusion principle a state can accomodate a maximum of two electrons with different quantum numbers, say one spin up $\left(m_s = \frac{1}{2}\right)$

the other one spin down $\left(m_s = -\frac{1}{2}\right)$. This number is governed by the rule $(2s + 1) =$

2. If we are dealing with spin 1 particles the total number of particles that a state can accommodate $= (2 \times 1 + 1) = 3$. Remember that this rule is applicable only to fermions.

The restriction on the number particle on the states brings change in the number of macrostates.

For example consider the distribution of 6 units of energy to a system containing 5 particles. If the particles are classical, we could see that there are totally 10

macrostates possible (see tabular column p. 12). If the particles are electrons each energy state can accommodate only two electrons. Thus in the tabular column macrostates 1, 2, 3, 6, 7, 8 and 10 are forbidden. That is the possible number of macrostates is only $(10 - 7) = 3$.

Finally we calculate the probability $P(\varepsilon)$ in quantum statistics and their functional form.

$$\text{We have } P(\varepsilon) = \frac{\sum_i N_i W_i}{N \sum_i W_i}$$

Where i runs over all macrostates. In quantum statistical mechanics the multiplicity in each macrostate is one i.e. $W_i = 1$

Particle is spin $\frac{1}{2}$

In our example there are only 3 macrostates. Which is shown below

Energy of the particles

Macrostate	0	1	2	3	4	5	6	Total energy
1	2	2	0	0	1	0	0	6
2	2	1	1	1	0	0	0	6
3	1	2	2	0	0	0	0	6

$$P(\varepsilon) = \frac{\sum_{i=1}^3 N_i W_i}{N \sum_i W_i}$$

$$P(\varepsilon) = \frac{N_1 W_1 + N_2 W_2 + N_3 W_3}{N (W_1 + W_2 + W_3)}$$

In quantum statistical mechanics

$$W_1 = W_2 = W_3 = 1$$

$$\therefore P(\varepsilon) = \frac{N_1 + N_2 + N_3}{N \cdot 3}, \quad N_1 + N_2 + N_3 = N \text{ total number}$$

$$P(0) = \frac{2+2+1}{5 \times 3} = \frac{1}{3} = 0.333$$

$$P(1) = \frac{2+1+2}{5 \cdot 3} = \frac{1}{3} = 0.333$$

$$P(2) = \frac{0+1+2}{5 \cdot 3} = \frac{1}{5} = 0.2$$

$$P(3) = \frac{0+1+0}{5 \cdot 3} = \frac{1}{15} = 0.067$$

$$P(4) = \frac{1+0+0}{5 \cdot 3} = \frac{1}{15} = 0.067$$

$$P(5) = \frac{0+0+0}{5 \cdot 3} = \frac{0}{15} = 0.000$$

$$P(6) = \frac{0+0+0}{5 \cdot 3} = \frac{0}{15} = 0.000$$

Plotting a graph between energy on the x-axis and probability $P(\varepsilon)$ on the Y-axis we get a graph shown in figure.

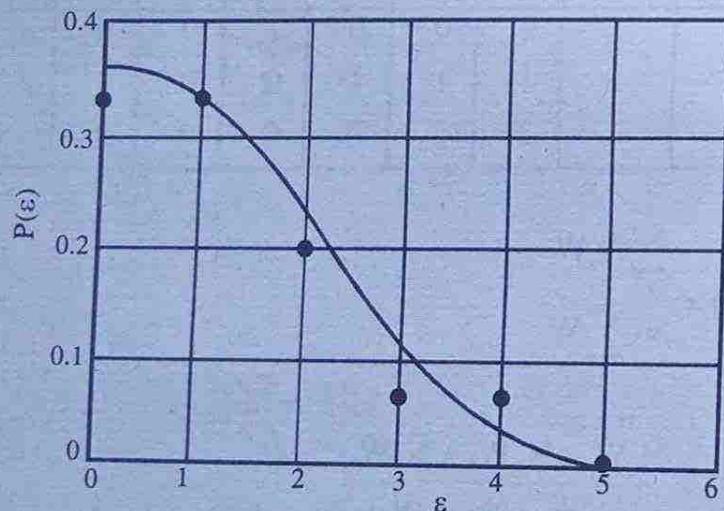


Figure 1.2: Probability versus energy graph for spin $\frac{1}{2}$ particles

The graph is not approximately exponential but flat near $\varepsilon = 0$ then drops rapidly to 0 for the high energies.

A rigorous mathematical calculation shows that

$$P(\varepsilon) = \frac{1}{Ae^{\beta\varepsilon} + 1}$$

If we neglect 1 in the denominator, the quantum statistical probability becomes analogous to classical statistical probability.

Probability for integral spin particles (photon or α - particles)

In general integral spin particles are called Bosons. Bosons do not obey Pauli's exclusion principle. Each energy state of the system can accommodate in any number of particles. In our example of 6 units of energy and 5 particles now which are bosons have 10 macrostates with equal multiplicities of one.

$$\text{We have } P(\varepsilon) = \frac{\sum_{i=1}^{10} N_i W_i}{N \sum_{i=1}^{10} N_i W_i}$$

$$P(\varepsilon) = \frac{\sum_{i=1}^{10} N_i}{N \sum_{i=1}^{10} W_i} \because W_i = 1, i = 1, 2, \dots, 10$$

From the table I (page 12)

$$P(0) = \frac{4+3+3+2+2+3+2+1+1+0}{5 \times 10}$$

$$P(0) = \frac{21}{50} = 0.420$$

$$P(1) = \frac{0+1+0+2+1+0+0+3+2+4}{5 \times 10}$$

$$P(1) = \frac{13}{50} = 0.260$$

$$P(2) = \frac{0+0+1+0+1+0+3+0+2+1}{5 \times 10}$$

$$P(2) = \frac{8}{50} = 0.160$$

$$P(3) = \frac{0+0+0+0+1+2+0+1+0+0}{5 \times 10}$$

$$P(3) = \frac{4}{50} = 0.080$$

$$P(4) = \frac{0+0+1+1+0+0+0+0+0+0}{5 \times 10}$$

$$P(4) = \frac{2}{50} = 0.040$$

$$P(5) = \frac{0+1+0+0+0+0+0+0+0+0}{5 \times 10}$$

$$P(5) = \frac{1}{50} = 0.020$$

$$P(6) = \frac{1+0+0+0+0+0+0+0+0+0}{5 \times 10}$$

$$P(6) = \frac{1}{50} = 0.020.$$

Plotting a graph between energy ε and the probability $P(\varepsilon)$, we get a graph shown in figure below.

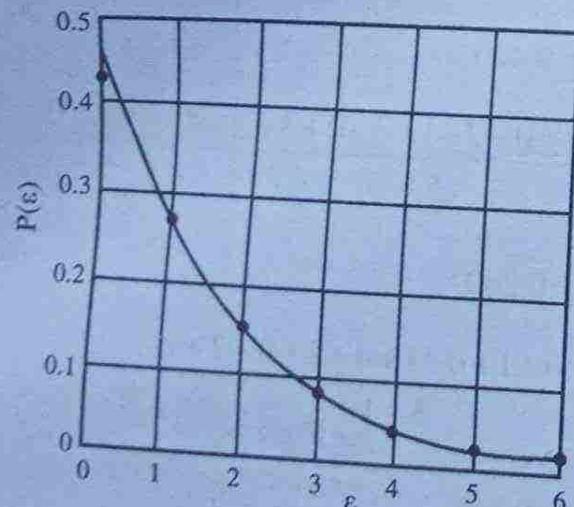


Figure 1.3: Probability versus energy for integral spin particles

From the plot it can be seen that the curve is approximately exponential but rises a bit more steeply at low energies. A rigorous mathematical calculation shows that probability is

$$P(\varepsilon) = \frac{1}{Ae^{\beta\varepsilon} - 1}$$

If we neglect one in the denominator the Boson probability is analogous to classical probability.

Note : It may be noted that the constant A appearing before the expressions of three probabilities are not the same. They are different constants.

Example 3

A system consists of 4 distinguishable simple harmonic oscillators each can have energy 0, ε , 2ε , 3ε , 4εetc. There is a constraint that the total energy is 4ε . Find the total number of microstates.

Solution

$$\text{We have } W_{\text{total}} = \frac{(N+Q-1)!}{Q!(N-1)!} = \frac{(4+4-1)!}{4!(4-1)!}$$

$$W_{\text{total}} = \frac{7!}{4!3!} = \frac{5 \times 6 \times 7}{1 \cdot 2 \cdot 3} = 35$$

OR

0	ε	2ε	3ε	4ε	$W = \frac{N!}{N_0! N_1! N_2! N_3! N_4! N_5!}$
3	0	0	0	1	$W_1 = 4$
2	1	0	1	0	$W_2 = 12$
2	0	2	0	0	$W_3 = 6$
1	2	1	0	0	$W_4 = 12$
0	4	0	0	0	$W_4 = 1$

$$\text{So } W_{\text{total}} = 4 + 12 + 6 + 12 + 1 = 35$$

Example 4

A gas has two particles a and b. How these particles can be arranged in 3 states 1, 2, 3 treating particles as a) classical b) having half integral c) having integral spin.

Solution

- a) As classical particle

1	2	3
a	b	-
b	a	-
ab	-	-
0	ab	-
0	-	ab
a	0	b
0	a	b
0	b	a
b	0	a

Totally there are nine arrangements. i.e., total number of microstates = 9. Using a simple formula we can calculate W. If there are N_i number of particles and g_i number of states, $W = g_i^{N_i} = 3^2 = 9$

- b) As half integral spin particles

Here $a = b \equiv a$

1	2	3
a	a	0
a	0	a
0	a	a

So there is only 3 microstates. For spin half particles, if there are N_i particles and g_i states then

$$W = \frac{g_i!}{N_i!(g_i - N_i)!} = \frac{3!}{2!(3-2)!} = 3$$

- c) As integral spin particles

Her $a = b \equiv a$. Being Bosons any number of particles can be accommodated in each energy state

1	2	3
a	a	0
a	0	a
0	a	a
aa	0	0
0	aa	0
0	0	aa

∴ The number of microstates = 6

$$\text{Using the formula } W = \frac{(N_i + g_i - 1)!}{N_i !(g_i - 1)!}$$

We can directly calculate this

$$W = \frac{(2+3-2)!}{2! 2!} = \frac{4!}{2! 2!} = 6$$

Example 5

A system of four oscillator like particles shares 8 units of energy. Particle can accept energy only in equal units, in which oscillator spacing is one unit.

- List the macrostates and for each macrostate give the number of microstates for distinguishable classical particles, indistinguishable quantum particles with integral spin and with half integral spin.
- Calculate the probability to find a particle with exactly 2 units of energy for each of the three different types of particles.

Solution

We have four particles and 8 units of energy.

Treating particles as classical

Macrostate possible	Energy of particles									Total energy
	0	1	2	3	4	5	6	7	8	
1	3	0	0	0	0	0	0	0	1	8
2	2	1	0	0	0	0	0	1	0	8
3	1	2	0	0	0	0	1	0	0	8
4	0	3	0	0	0	1	0	0	0	8
5	2	0	0	1	0	1	0	0	0	8
6	2	0	1	0	0	0	1	0	0	8
7	0	1	2	1	0	0	0	0	0	8
8	1	1	1	0	0	1	0	0	0	8
9	1	1	0	1	1	0	0	0	0	8
10	0	2	1	0	1	0	0	0	0	8
11	1	0	2	0	1	0	0	0	0	8
12	2	0	0	0	2	0	0	0	0	8
13	1	0	1	2	0	0	0	0	0	8
14	0	2	0	2	0	0	0	0	0	8
15	0	0	4	0	0	0	0	0	0	8

There are no more possibilities. Thus we have totally 15 macrostates.

In each macrostate we have to calculate the multiplicity W .

$$\text{In general } W_i = \frac{N!}{N_0! N_1! N_2! N_3! N_4! N_5! N_6! N_7! N_8!}$$

We can calculate one by one.

$$W_1 = \frac{4!}{3! 1!} = 4, \quad (\because 0! = 1 \text{ and } 1! = 1)$$

$$W_2 = \frac{4!}{2!} = 12,$$

$$W_3 = \frac{4!}{1! 2! 1!} = 12,$$

$$W_4 = \frac{4!}{3! 1!} = 4,$$

$$W_5 = \frac{4!}{2!} = 12,$$

$$W_6 = \frac{4!}{2!} = 12,$$

$$W_7 = \frac{4!}{2!} = 12,$$

$$W_8 = 4! = 24$$

$$W_9 = \frac{4!}{2!} = 24,$$

$$W_{10} = \frac{4!}{2!} = 12,$$

$$W_{11} = \frac{4!}{2! 1!} = 12,$$

$$W_{12} = \frac{4!}{2!2!} = 6,$$

$$W_{13} = \frac{4!}{2!} = 12,$$

$$W_{14} = \frac{4!}{2!2!} = 6,$$

$$W_{15} = \frac{4!}{4!} = 1,$$

\therefore Over all total multiplicity

$$W_{\text{total}} = 4 + 12 + 12 + 4 + 12 + 12 + 24 + 24 + 12 + 12 + 12 + 6 + 12 + 6 + 1$$

$$W_{\text{total}} = 165$$

There is another nice way to calculate W_{total} . If there are N particles sharing Q units of energy, then

$$W_{\text{total}} = \frac{(N+Q-1)!}{Q!(N-1)!} = \frac{(4+8-1)}{8!(4-1)!} = \frac{11!}{8! 3!}$$

$$W_{\text{total}} = 165$$

b) Probability $P(\varepsilon)$

$$\text{We have } P(\varepsilon) = \frac{\sum_i N_i W_i}{N \sum_i W_i}$$

i runs over all macrostates

$$P(\varepsilon) = \frac{\sum_{i=1}^{15} N_i W_i}{N \sum_{i=1}^{15} W_i}$$

$$\therefore P(2) = \frac{0 \times 4 + 0 \times 12 + 0 \times 12 + 0 \times 4 + 0 \times 12 + 1 \times 12 + 2 \times 12 + 1 \times 24 + 0 \times 24 + 1 \times 12 + 2 \times 12 + 0 \times 6 + 1 \times 12 + 0 \times 6 + 4 \times 1}{4 \times 165}$$

$$P(2) = \frac{12 + 24 + 24 + 12 + 24 + 12 + 4}{4 \times 165} = \frac{112}{4 \times 165}$$

$$P(2) = 0.170$$

Treating particles as having half integral spin

Half integral particles obey Pauli's exclusion principle. Hence each energy state can accommodate only two particles at maximum. From the table we can see that macrostates 1, 4 and 15 are not allowed. Hence total number of macrostates possible is $(15 - 3) = 12$ since particle is quantum, multiplicity of each macrostate is 1. The total number of microstates is 12.

$$P(\varepsilon) = \frac{\sum_{i=1}^{12} N_i W_i}{N \sum_{i=1}^{12} W_i} = \frac{\sum_{i=1}^{12} N_i}{4 \times 12} \quad W_i = 1$$

$$\therefore P(2) = \frac{N_1 + N_2 + N_3 + N_4 + N_5 + N_6 + N_7 + N_8 + N_9 + N_{10} + N_{11} + N_{12}}{48}$$

Collecting only the number of particles with energy 2 units.

$$N_1 = 0, N_2 = 0, N_3 = 0, N_4 = 1, N_5 = 0, N_6 = 1, N_7 = 0, N_8 = 1, N_9 = 2,$$

$$N_{10} = 0, N_{11} = 1 \text{ and } N_{12} = 2$$

$$P(2) = \frac{0+0+0+1+0+1+0+1+2+0+1+2}{48}$$

$$P(2) = \frac{8}{48} = 0.167$$

Treating particles as having integral spin

Integral spin particles can accommodate any number of particles in each energy state. Hence the number of macrostates is obviously 15. Since this being quantum particles, the multiplicity of each macrostate is one.

\therefore The total number of microstate is 15. Collecting the number of particles from each macrostate having 2 units of energy we get

$$N_1 = 0, N_2 = 0, N_3 = 0, N_4 = 0, N_5 = 0, N_6 = 1, N_7 = 2, N_8 = 1, N_9 = 0, N_{10} = 1,$$

$$N_{11} = 2, N_{12} = 0, N_{13} = 1, N_{14} = 0, \text{ and } N_{15} = 4$$

$$P(\varepsilon) = \frac{\sum_{i=1}^{15} N_i W_i}{N \sum_{i=1}^{15} W_i} \quad \begin{aligned} W_i &= 1 \\ \sum_{i=1}^{15} W_i &= 15 \end{aligned}$$

$$P(\varepsilon) = \frac{\sum_{i=1}^{15} N_i}{4 \times 15}$$

$$P(2) = \frac{0+0+0+0+0+1+2+1+0+1+2+0+1+0+4}{60}$$

$$P(2) = \frac{12}{60} = \frac{1}{5} = 0.20.$$

Example 6

A system containing 4 electrons and 5 α -particles. Calculate the total number of microstates.

Solution

Electron is a spin $\frac{1}{2}$ particle, each electron has $(2s+1)$ states $= 2 \times \frac{1}{2} + 1 = 2$ states.

\therefore Number of microstates of 4 electrons $= 2^4 = 16$

α -particle is a spin 1 particle, each particle has $2 \times 1 + 1 = 3$ states

\therefore Number of microstates of 5 α -particles $= 3^5 = 243$.

\therefore Over all number of microstates $= 243 \times 16$
 $= 3888$

Density of states

We found that how the multiplicity of a state determines the probability to find a system in that state. There we considered only simple systems and containing only few number of particles. Now we are going to extend this concept to more complicated systems.

Let us consider a system (classical or quantum) composed of a large number of particles that can exist in many different ways. The relative probability for the particles to have energy ε is given by the distribution function $P(\varepsilon) \propto e^{-\beta\varepsilon} = f(\varepsilon)$ where

β is found to be $\frac{1}{kT}$ (k is the Boltzmann's constant and T is the temperature in kelvin).

The distribution function $f(\varepsilon)$ tells us that when the energy of the particle ε is large, the particle is less likely to be found in the system. Since $f(\varepsilon)$ depends upon the temperature of the system so also probability. If $\varepsilon \gg kT$, the probability becomes more and more less probable.

Here our aim is to calculate the number of particles with any given value of energy ε . Thus number is partly given by $f(\varepsilon)$. The other factor that has to be taken into account is the multiplicity of microstate. In effect to find the number of occupied states we combine the number of available states with the probability that each state is occupied.

Calculation of number of available states at energy ε

(i) When the energy states are discrete and individually observable.

In this case the number of available states at the energy ε is the degeneracy of the state (d) and the probability of the state is $f(\varepsilon)$.

∴ The number of particles (N_n) in the system with energy ε_n and probability $f(\varepsilon_n)$ is given by

$$N_n = d_n f(\varepsilon_n) \quad \dots \dots (8)$$

∴ The total number of particles in the system

$$N = \sum N_n = \sum_n d_n f(\varepsilon_n) \quad \dots \dots (9)$$

where the summation is carried over all the energy states.

Remember that for hydrogen gas the degeneracy is $2n^2$, for rotational excited

states in a molecule is $(2l + 1)$, where l is the orbital quantum number, and for electrons it is $(2s + 1)$ and so on.

(ii) For energy states are continuous and cannot observe the individual states.

This happens when the number of particles is exceedingly large. In this case the energy states are so closed so that we cannot observe them as separate. In this context we consider only the number of energy states in an interval between at energies ε and $\varepsilon + d\varepsilon$. For this analysis we treat ε as a continuous variable so that we will able to replace summation by integration.

Density of states $g(\varepsilon)$

It is defined as the number of available states per unit volume in the interval $d\varepsilon$ energy ε . This is symbolically represented as $g(\varepsilon)d\varepsilon$.

The total number of states in the interval $d\varepsilon$ is

$$dN = N(\varepsilon)d\varepsilon = Vg(\varepsilon)f(\varepsilon)d\varepsilon \quad \dots\dots (10)$$

$N(\varepsilon)$ is not the total number of particles but it is the number of particles with energy ε .

The total number of particles in system can be obtained by integrating the above expression.

$$\therefore N = \int_0^{\infty} N(\varepsilon)d\varepsilon = V \int_0^{\infty} g(\varepsilon)f(\varepsilon)d\varepsilon \quad \dots\dots (11)$$

Here it is taken that energy (ε) of the particle varies from 0 to ∞ .

Density of states in a gas of particles

Here we calculate the density of states in a gas of particles such as electrons or molecules. This calculation is necessary in our further studies. For example suppose we study the thermionic emission by statistical analysis. The space around a hot filament is filled with a cloud of electrons. To study the properties of thermionic emission first of all we have to calculate the density of states for further development of the theory. Another example is suppose we want to study the properties of metals by statistical analysis. Metal consists of large number of free electrons which are responsible for all properties exhibited by metals. For the statistical analysis of the system first of all we have to calculate the density of states of the system.

Calculation of $g(\epsilon)$

The basis of our calculation is the particle (electron) trapped in a cubical box of side L . The energy of the particle is given by

$$\epsilon = \frac{p^2}{2m} = \frac{(p_x^2 + p_y^2 + p_z^2)}{2m} = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

$$\epsilon = \frac{\hbar^2 n^2}{8mL^2} \text{ where } n^2 = n_x^2 + n_y^2 + n_z^2$$

we can see that the number of energy states with a particular value of ϵ depends on how many combinations of n_x , n_y , n_z result in the same value of ϵ . Since we are dealing with almost a continuum of energy levels, we may construct a space of points represented by the values of n_x , n_y and n_z and let each point with integer values of the coordinates represent an energy state.

To find the number of energy states, construct a coordinate system with n_x , n_y and n_z as axes. The points with same value of ϵ lie on a spherical surface of radius $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$. The points with energies between ϵ and $\epsilon + d\epsilon$ lie within a spherical shell between the radius n and $n + dn$.

$$\text{The number of available states within a radius } n = \frac{1}{8} \left(\frac{4}{3} \pi n^3 \right)$$

The factor $\frac{1}{8}$ accounts for the fact that only positive integer values of n_x , n_y and n_z are allowed and thus only one octant of the sphere alone be considered.

The number of states within a sphere of radius $n + dn = \frac{1}{8} \frac{4}{3} (n + dn)^3$

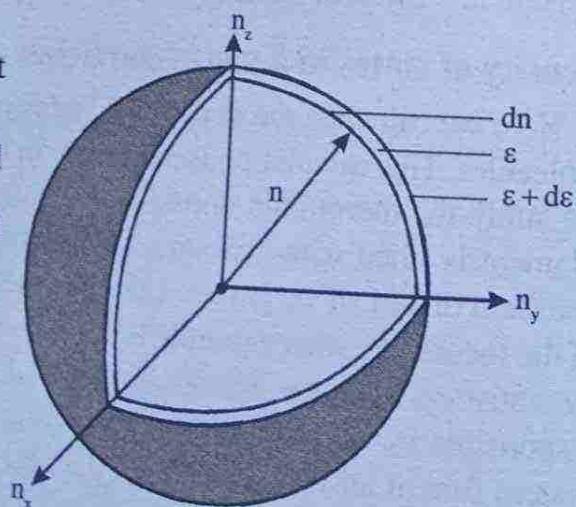


Figure 1.4: Density of states

∴ The number of energy states having energy values ϵ and $\epsilon + d\epsilon$,

$$\begin{aligned} &= \frac{1}{8} \frac{4}{3} \pi (n + dn)^3 - \frac{1}{8} \frac{4}{3} \pi n^3 \\ &= \frac{\pi}{6} [(n + dn)^3 - n^3] \\ &= \frac{\pi}{6} (3n^2 dn + 3ndn^2 + dn^3) \end{aligned}$$

Neglecting dn^2 and dn^3 , we get

$$\approx \frac{\pi}{2} n^2 dn$$

∴ The energy states per unit volume

$$g(n)dn = \frac{\text{Energy states}}{\text{Volume}} = \frac{\pi n^2 dn}{2V}$$

But each state is degenerate with degeneracy $(2s+1)$ for fermions.

$$\therefore g(n)dn = (2s+1) \frac{\pi n^2 dn}{2V}$$

If our particle is electron $s = \frac{1}{2}$

$$\therefore g(n)dn = \frac{\pi n^2 dn}{V} - \text{for spin } \frac{1}{2} \text{ particles}$$

$$\text{We have } \epsilon = \frac{h^2 n^2}{8mL^2} \text{ gives } n^2 = \frac{8mL^2}{h^2} \epsilon$$

$$\text{or } n = \sqrt{8m} \frac{L}{h} \epsilon^{\frac{1}{2}}$$

$$dn = \sqrt{8m} \frac{L}{h} \epsilon^{-\frac{1}{2}} d\epsilon$$

$$= \sqrt{2m} \frac{L}{h} \epsilon^{-\frac{1}{2}} d\epsilon$$

Substituting the value of n^2 and n in the expression for $g(n)dn$, we get

$$g(n)dn = \frac{\pi}{V} \frac{8mL^2}{h^2} \varepsilon \sqrt{2m} \frac{L}{h} \varepsilon^{-\frac{1}{2}} d\varepsilon$$

The volume of the cube $V = L^3$, we started with

$$g(n)dn = \frac{8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} \varepsilon^{\frac{1}{2}} d\varepsilon$$

Now we change the symbolic representation of density of states $g(n)dn$ to $g(\varepsilon)d\varepsilon$, since energy states is expressed in terms of energy on the R.H.S.

i.e.
$$g(\varepsilon)d\varepsilon = \frac{8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} \varepsilon^{\frac{1}{2}} d\varepsilon$$

In general
$$g(\varepsilon) = \frac{4\sqrt{2}\pi(2s+1)m^{\frac{3}{2}}}{h^3} \varepsilon^{\frac{1}{2}} \quad \dots\dots (12)$$

Note : For classical particles, the degeneracy is 1 and $h = h_0$

$$\therefore g(\varepsilon)d\varepsilon = \frac{4\sqrt{2}\pi m^{\frac{3}{2}}}{h_0^3} \varepsilon^{\frac{1}{2}} d\varepsilon$$

Density of states in terms of momentum

We have
$$g(\varepsilon)d\varepsilon = \frac{4\sqrt{2}\pi(2s+1)m^{\frac{3}{2}}}{h^3} \varepsilon^{\frac{1}{2}} d\varepsilon$$

Using $\varepsilon = \frac{p^2}{2m}$ $d\varepsilon = \frac{pd़}{m}$

$$\therefore g(\varepsilon)d\varepsilon = \frac{4\sqrt{2}\pi(2s+1)m^{\frac{3}{2}}}{h^3} \frac{p}{(2m)^{\frac{1}{2}}} \frac{pd़}{m}$$

$$g(\varepsilon)d\varepsilon = \frac{4\pi(2s+1)p^2d़}{h^3}$$

i.e.
$$g(p)dp = \frac{4\pi(2s+1)p^2d़}{h^3} \quad \dots\dots (13)$$

This is called density of momentum states. This is the simplest formula, you can apply this anywhere.

$$\text{For classical particles } g(p)dp = \frac{4\pi p^2 dp}{h_0^3} \quad (\because 2s+1=1)$$

For classical particle

$$(i) \text{ Density of states in 3D, } g(p)dp = \frac{4\pi p^2 dp}{h_0^3}$$

$$(ii) \text{ Density of states in 2D, } g(p)dp = \frac{2\pi pdp}{h_0^2}$$

$$(iii) \text{ Density of states in 1D, } g(p)dp = \frac{dp}{h_0}$$

If the particle has degeneracy, multiply density of states with corresponding degeneracy and replace h_0 by Planck's constant h .

Density of states in a gas of photons

To find the density of photons we need not go for all the procedures that followed in the last section. We simply started with

$$g(p)dp = \frac{4\pi(2s+1)p^2 dp}{h^3}$$

For photons $s=1$, \therefore The degeneracy is found to be $= 2 \times 1 + 1 = 3$. However photon has got only two since third state is not permitted. These are actually leading to two polarisations of electromagnetic waves.

$$\therefore g(p)dp = \frac{8\pi p^2 dp}{h^3}$$

$$\text{For a photon } p = \frac{\epsilon}{c} \quad \therefore \quad dp = \frac{d\epsilon}{c}$$

$$g(p)dp = \frac{8\pi \epsilon^2}{h^3 c^2} \frac{d\epsilon}{c}$$

$$g(\varepsilon)d\varepsilon = \frac{8\pi\varepsilon^2d\varepsilon}{h^3c^2}$$

i.e., the density of states of photon gas

$$g(\varepsilon) = \frac{8\pi\varepsilon^2}{h^3c^2} \quad \dots\dots (14)$$

Example 7

Calculate the density of states of helium gas within an interval of 0.0002 eV at the most probable molecular energy of 0.0086 eV at a temperature of 200K.

$$m_{He} = 3727 \text{ MeV}$$

Solution

$$d\varepsilon = 0.0002 \text{ eV}, \quad \varepsilon = 0.0086 \text{ eV}, \quad m_{He} = 3727 \text{ MeV}$$

$$\text{Density of states, } g(\varepsilon)d\varepsilon = \frac{4\pi\sqrt{2}m^{\frac{3}{2}}}{h^3} \varepsilon^{\frac{1}{2}}d\varepsilon \quad (\text{Treated as classical particle})$$

$$\text{The above equation can be re-written as } g(\varepsilon)d\varepsilon = \frac{4\pi\sqrt{2}(mc^2)^{\frac{3}{2}}}{(hc)^3} \varepsilon^{\frac{1}{2}}d\varepsilon$$

Putting the values $mc^2 = 3727 \times 10^6 \text{ eV}$, $\varepsilon = 0.0086 \text{ eV}$ and $hc = 1240 \text{ eV.nm}$

$$g(\varepsilon)d\varepsilon = \frac{4\pi\sqrt{2}(3727 \times 10^6 \text{ eV})^{\frac{3}{2}} \times (0.0086 \text{ eV})^{\frac{1}{2}} \times (0.0002 \text{ eV})}{(1240 \text{ nm eV})^3}$$

$$g(\varepsilon)d\varepsilon = \frac{4\pi\sqrt{2} \times 3727^{\frac{3}{2}} \times 10^9 \times 0.0086^{\frac{1}{2}} \times 0.0002}{1240^3 \text{ nm}^3}$$

$$g(\varepsilon)d\varepsilon = 39.3 \text{ nm}^{-3}$$

$g(\varepsilon)d\varepsilon$ is the number of states per unit volume (1m^3)
Converting into m^3

$$g(\varepsilon)d\varepsilon = \frac{39.3}{(10^{-9}\text{m})^3} = 39.3 \times 10^{27} \text{ m}^{-3}$$

Example 8

A proton is confined to move in a nucleus with radius 10^{-14} m. Its momentum cannot exceed 10^{-19} kg ms $^{-1}$. Calculate the over all number of states.

Solution

$$p = 10^{-19} \text{ kg ms}^{-1}, r = 10^{-14} \text{ m}$$

We have $g(p)dp = \frac{4\pi p^2 dp}{h^3}$ integrating we get, over all density of states per unit volume

$$\begin{aligned} &= \int_0^{p_{\max}} \frac{4\pi p^2 dp}{h^3} \\ &= \frac{4\pi}{3} \frac{p_{\max}^3}{h^3} \\ &= \frac{4 \times 3.14 \times (10^{-19})^3}{3 \times (6.64 \times 10^{-34})^3} \\ &= \frac{4 \times 3.14 \times 10^{45}}{3 \times 6.64^3} = 1.43 \times 10^{43} \end{aligned}$$

$$\therefore \text{over all number of states} = 1.43 \times 10^{43} \times V$$

$$\begin{aligned} &= 1.43 \times 10^{43} \times \frac{4}{3} \pi r^3 \\ &= 1.43 \times 10^{43} \times \frac{4}{3} 3.14 \times (10^{-14})^3 \\ &\approx 60 \end{aligned}$$

Example 9

The universe is filled with photons left over from the big bang that today have an energy of about 2×10^{-4} eV corresponding to a temperature of 2.7 K. Calculate the density of states of photons in an interval of 10^{-5} eV.

Solution

$$\epsilon = 2 \times 10^{-4} \text{ eV}, d\epsilon = 10^{-5} \text{ eV}$$

We have $g(\varepsilon)d\varepsilon = \frac{8\pi\varepsilon^2d\varepsilon}{h^3c^3}$

$$= \frac{8 \times 3.14 \times (2 \times 10^{-4} \text{ eV})^2 \times 10^{-5} \text{ eV}}{(1240 \text{ eV nm})^3}$$

$$g(\varepsilon)d\varepsilon = \frac{8 \times 3.14 \times 4 \times 10^{-8} \times 10^{-5}}{1240^3 \text{ nm}^3}$$

$$g(\varepsilon)d\varepsilon = \frac{8 \times 3.14 \times 4 \times 10^{-13}}{1240^3 \times (10^{-9} \text{ m})^3}$$

$$= \frac{8 \times 3.14 \times 4 \times 10^{14}}{1240^3 \text{ m}^3}$$

$$= 5.29 \times 10^6 \text{ m}^{-3}.$$

Maxwell-Boltzmann distribution functions

To calculate the total number of particles in a system we require not only density of states but also distribution function $f(\varepsilon)$. Depending upon the nature of the system of particles such as classical, fermions or bosons we have three types of corresponding distribution functions. For classical particles the distribution function is called Maxwell-Boltzmann distribution function denoted by $f(\varepsilon)$. For fermions (half integral spin) the distribution function is called Fermi-Dirac distribution function denoted by $f_{FD}(\varepsilon)$. For bosons (integral spin) the distribution function is called Bose-Einstein distribution function denoted by $f_{BE}(\varepsilon)$. Distribution function tells us how the particles are distributed among different energy states of the system. Recall that our distribution functions are probability distribution functions.

Maxwell-Boltzmann distribution

Here our aim is to calculate the number of particles in a classical system in which the density is relatively low. This means that in such systems the average spacing between the particles is large compared with their de-Broglie wavelength. The individual particles may have quantised energy levels but the overall system does not show quantum behaviour. The Maxwell-Boltzmann distribution is given by

$$f_{MB}(\varepsilon) = A^{-1} e^{-\frac{\varepsilon}{kT}} \quad \dots\dots (16)$$

The constant is taken as A^{-1} in order to have the same form for all the three distribution functions.

Now we will apply this to calculate the number of particles in a classical system.

Consider an ideal gas enclosed in a container of volume V . Let N be the number of molecules in the container at temperature T . Let $N(\varepsilon)$ be the number of molecules in between energy ε and $\varepsilon + d\varepsilon$. We know that (Recall equation 10)

$$N(\varepsilon)d\varepsilon = V g(\varepsilon) f_{MB}(\varepsilon) d\varepsilon \quad \dots (17)$$

Substituting for $g(\varepsilon)$ from equation 12 and $f_{MB}(\varepsilon)$ from equation 16, we get

$$N(\varepsilon)d\varepsilon = \frac{V 4\sqrt{2}\pi m^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} (2s+1) A^{-1} e^{-\frac{\varepsilon}{kT}}}{h^3} \quad \dots (18)$$

Evaluation of the constant A^{-1}

$N(\varepsilon)d\varepsilon$ gives the number of particles in between energy ε and $\varepsilon + d\varepsilon$

\therefore The number of particles

$$N = \int_0^\infty N(\varepsilon)d\varepsilon$$

Since this being a classical system the variation of energy can be taken to be 0 to ∞ .

$$N = \frac{V 4\sqrt{2}\pi m^{\frac{3}{2}} (2s+1) A^{-1}}{h^3} \int_0^\infty \varepsilon^{\frac{1}{2}} e^{-\frac{\varepsilon}{kT}} d\varepsilon$$

Using the standard integral

$$\int_0^\infty x^n e^{-ax} dx = n!(a)^{-n-1}$$

$$\begin{aligned} \therefore \int_0^\infty \varepsilon^{\frac{1}{2}} e^{-\frac{\varepsilon}{kT}} d\varepsilon &= \left(\frac{1}{2} \right)! \left(\frac{1}{kT} \right)^{-\frac{1}{2}-1} \quad \left(\frac{1}{2}! = \frac{\sqrt{\pi}}{2} \right) \\ &= \frac{\sqrt{\pi}}{2} (kT)^{\frac{3}{2}} \end{aligned}$$

$$N = \frac{V 2\sqrt{2}\pi^{\frac{3}{2}} m^{\frac{3}{2}} (2s+1) (kT)^{\frac{3}{2}} A^{-1}}{h^3}$$

$$N = \frac{V}{h^3} (2s+1) (2\pi mkT)^{\frac{3}{2}} A^{-1}$$

or $A^{-1} = \frac{Nh^3}{V(2s+1)(2\pi mkT)^{\frac{3}{2}}} \dots\dots (19(a))$

Substituting this in equation 18 we get

$$N(\varepsilon)d\varepsilon = \frac{V4\sqrt{2}\pi m^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}(2s+1)e^{-\frac{kT}{\varepsilon}}}{h^3} \times \frac{Nh^3d\varepsilon}{V(2s+1)(2\pi mkT)^{\frac{3}{2}}}$$

$$N(\varepsilon)d\varepsilon = \frac{2N}{\sqrt{\pi}(kT)^{\frac{3}{2}}} \varepsilon^{\frac{1}{2}} e^{-\frac{kT}{\varepsilon}} d\varepsilon \dots\dots (19)$$

This is called Maxwell-Boltzmann energy distribution law.

The distribution of number of particles $N(\varepsilon)$ with energy ε is shown in figure below.

It can be seen from the graph that $N(\varepsilon)$ increases with energy. It rises to a maximum value, the corresponding energy is called most probable energy (ε_p). It is found to be $\frac{1}{2}kT$ (see example 9).

After reaching maximum, $N(\varepsilon)$ decreases to zero as energy increases. This shows that it is rare to find a molecule with energy much greater than kT . The number of molecules dN within the energy can be calculated by the equation 19. Moreover the average energy of the gas molecules can be calculated, it is found to be $\varepsilon_m = \frac{3}{2}kT$ (see example 10). This is found to be in exact agreement with experimental result. This gives us a justification for the development of statistical analysis.

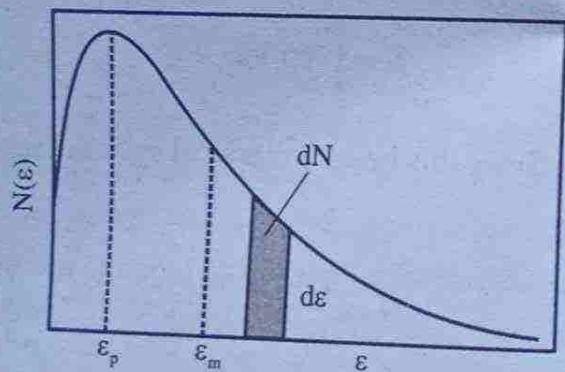


Figure 1.5
The Maxwell-Boltzmann energy distribution for molecules, showing the most probable energy ε_p and the mean energy ε_m . The shaded strip represents the number of molecules dN with energies between ε and $\varepsilon + d\varepsilon$.

Note: The expression we derived for probability $p(\varepsilon)$ enables us to calculate the relative population of particles in various energy states. Using $p(\varepsilon) \propto d e^{-\frac{\varepsilon}{kT}}$, where d is the degeneracy of each energy level. (see example 11 and 12).

Example 9

Show that the most probable energy $\varepsilon_p = \frac{1}{2}kT$ in the case of Maxwell-Boltzmann distribution.

Solution

$$\text{We have } N(\varepsilon) = \frac{2N}{\sqrt{\pi(kT)^{\frac{3}{2}}}} \varepsilon^{\frac{1}{2}} e^{-\frac{\varepsilon}{kT}}$$

To find the maximum of $N(\varepsilon)$, differentiate the above with respect to ε and put equal to zero.

$$\frac{dN(\varepsilon)}{d\varepsilon} = \frac{2N}{\sqrt{\pi(kT)^{\frac{3}{2}}}} \left[\varepsilon^{\frac{1}{2}} e^{-\frac{\varepsilon}{kT}} - \frac{1}{kT} + \frac{1}{2} \varepsilon^{-\frac{1}{2}} e^{-\frac{\varepsilon}{kT}} \right]$$

$$\frac{dN(\varepsilon)}{d\varepsilon} = 0 \text{ gives } \varepsilon = \varepsilon_p$$

$$0 = -\frac{\varepsilon_p^{\frac{1}{2}} e^{-\frac{\varepsilon_p}{kT}}}{kT} + \frac{1}{2} \varepsilon_p^{-\frac{1}{2}} e^{-\frac{\varepsilon_p}{kT}}$$

$$\text{or } \frac{\varepsilon_p^{\frac{1}{2}}}{kT} = \frac{1}{2} \varepsilon_p^{-\frac{1}{2}}$$

$$\varepsilon_p = \frac{1}{2} kT$$

Example 10

Show that the average energy of gas molecules obeying Maxwell-Boltzmann distribution is $\varepsilon_m = \frac{3}{2}kT$

Solution

Total energy of the whole gas molecules

$$E = \int_0^{\infty} N(\varepsilon) \varepsilon d\varepsilon$$

substituting for $N(\varepsilon)$, we get

$$E = \int_0^{\infty} \frac{2N}{\sqrt{\pi(kT)^{\frac{3}{2}}}} \varepsilon^{\frac{3}{2}} e^{-\frac{\varepsilon}{kT}} d\varepsilon$$

Using the standard integral $\int_0^{\infty} x^n e^{-ax} dx = n! (a)^{-n-1}$

$$\begin{aligned} \int_0^{\infty} \varepsilon^{\frac{3}{2}} e^{-\frac{\varepsilon}{kT}} d\varepsilon &= \left(\frac{3}{2}\right)! \left(\frac{1}{kT}\right)^{-\frac{3}{2}-1} \\ &= \frac{3}{2} \frac{1}{2} \sqrt{\pi} (kT)^{\frac{5}{2}} \quad \left(\frac{3}{2}! = \frac{3}{2} \frac{1}{2} \sqrt{\pi} \right) \end{aligned}$$

$$\therefore E = \frac{2N}{\sqrt{\pi(kT)^{\frac{3}{2}}}} \frac{3}{2} \frac{1}{2} \sqrt{\pi} (kT)^{\frac{5}{2}}$$

$$E = \frac{3}{2} N k T$$

$$\text{or } \frac{E}{N} = \frac{3}{2} k T$$

$$\varepsilon_m = \frac{3}{2} k T$$

Example 11

Nitrogen gas consists of a sequence of vibrating excited states with energies $(n + \frac{1}{2})\hbar\omega$, $n = 0, 1, 2, \dots$. If the level spacing is 0.3eV. What is the relative population of first excited state ($n = 1$) and the ground state ($n = 0$). $T = 1000\text{ K}$, $k = 8.625 \times 10^{-5} \text{ eVK}^{-1}$. Degeneracy = 1

Solution

We have $p(\varepsilon) \propto e^{-\beta\varepsilon}$

For the first excited state $n = 1$

$$\therefore \varepsilon = \left(n + \frac{1}{2} \right) \hbar\omega$$

$$\varepsilon_1 = \frac{3}{2} \hbar\omega$$

For the ground state $n = 0$

$$\varepsilon_0 = \frac{1}{2} \hbar\omega$$

$$\therefore p(\varepsilon_1) \propto e^{-\beta\varepsilon_1}$$

$$p(\varepsilon_0) \propto e^{-\beta\varepsilon_0}$$

$$\frac{p(\varepsilon_1)}{p(\varepsilon_0)} = \frac{e^{-\beta\varepsilon_1}}{e^{-\beta\varepsilon_0}} = e^{-\beta(\varepsilon_1 - \varepsilon_0)}$$

$$= e^{-\frac{(\varepsilon_1 - \varepsilon_0)}{kT}}$$

$$\varepsilon_1 - \varepsilon_0 = 0.3 \text{ eV}$$

$$k = 8.625 \times 10^{-5} \text{ eV K}^{-1}$$

$$T = 1000 \text{ K}$$

$$\frac{p(\varepsilon_1)}{p(\varepsilon_0)} = e^{-\frac{0.3 \text{ eV}}{8.625 \times 10^{-5} \text{ eV K}^{-1} \times 1000 \text{ K}}}$$

$$\frac{p(\varepsilon_1)}{p(\varepsilon_0)} = e^{-\frac{0.3 \times 10^2}{8.625}} = e^{-3.478} = 0.031$$

Example 12

In a gas of atomic hydrogen at room temperature 293 K what is the number of atoms in the first excited state at $\varepsilon = 10.2 \text{ eV}$, expressed as a ratio to the number in the ground state. b) At what temperature would we expect to find $\frac{1}{10}$ as many atoms in the first excited state as in the ground state.

Solution

We have $N \propto d e^{-\beta \epsilon}$

$$N_1 \propto d_1 e^{-\beta \epsilon_1}$$

$$N_2 \propto d_2 e^{-\beta \epsilon_2}$$

$$\frac{N_2}{N_1} = \frac{d_2}{d_1} e^{-\beta(\epsilon_2 - \epsilon_1)}$$

The degeneracy of hydrogen atom is $2n^2$

$$d_1 = 2 \times 1^2 = 2$$

$$d_2 = 2 \times 2^2 = 8$$

$$\epsilon_2 - \epsilon_1 = 10.2 \text{ eV}$$

$$k = 8.625 \times 10^{-5} \text{ eVK}^{-1}$$

$$T = 293 \text{ K}$$

$$\therefore \frac{N_2}{N_1} = \frac{8}{2} e^{-\frac{10.2 \text{ eV}}{8.625 \times 10^{-5} \text{ eVK}^{-1} \times 293 \text{ K}}}$$

$$\frac{N_2}{N_1} = 4e^{-404}, \text{ Let } e^{-404} = 10^x \text{ gives } x = -175.45$$

$$\frac{N_2}{N_1} = 4 \times 10^{-175.42}$$

$$\frac{N_2}{N_1} = 4 \times 10^{-175} \cdot 10^{-0.45} = 1.419 \times 10^{-175}$$

b) $\frac{N_2}{N_1} = \frac{1}{10} = 0.1$ given. $T = ?$

Using $\frac{N_2}{N_1} = 4e^{-\frac{\epsilon_2 - \epsilon_1}{kT}}$

$$\frac{1}{10} = 4e^{-\frac{10.2}{kT}}$$

$$\frac{1}{40} = e^{-\frac{10.2}{kT}}$$

or $e^{\frac{10.2}{kT}} = 40$

$$\frac{10.2}{kT} = \ln 40$$

$$kT = \frac{10.2}{\ln 40} = \frac{10.2}{3.69} = 2.76 \text{ eV}$$

$$\therefore T = \frac{2.76}{k} = \frac{2.76}{8.625 \times 10^{-5}} = \frac{2.76}{8.625} \times 10^4$$

$$T = 3.2 \times 10^4 \text{ K}$$

Distribution of molecular speeds

The number of molecules with energy in between ε and $\varepsilon + d\varepsilon$ is given by

$$N(\varepsilon)d\varepsilon = \frac{2N}{\sqrt{\pi(kT)^{\frac{3}{2}}}} \varepsilon^{\frac{1}{2}} e^{-\frac{\varepsilon}{kT}} d\varepsilon$$

Using $\varepsilon = \frac{1}{2}mv^2$, $d\varepsilon = mvdv$ in the above equation, we get

$$N(\varepsilon)d\varepsilon = \frac{2N}{\sqrt{\pi(kT)^{\frac{3}{2}}}} \left(\frac{1}{2}mv^2 \right)^{\frac{1}{2}} e^{-\frac{mv^2}{2kT}} mv dv$$

Now the number particles with energy ε is written as a function of v , we have

$$N(v)dv = N \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} dv \quad \dots \dots (20)$$

This gives the number of particles with speeds in the interval dv at v .

This equation (20) is called Maxwell-Boltzmann speed distribution law.

Discussion

Case (i)

If $v = 0$

$$N(v) = 0$$

It means that no molecule has zero speed

Case (ii)

For small value of v

$$\frac{mv^2}{2kT} \ll 1 \text{ and } e^{-\frac{mv^2}{2kT}} \approx 1$$

$$\therefore N(v) \propto v^2$$

Thus, value $N(v)$ increases parabolically with increase of v and attains a maximum value for a particular v called most probable speed.

Case (iii)

For large value of v

$\frac{mv^2}{2kT} \gg 1$ and the exponential term $\left(e^{-\frac{mv^2}{2kT}} \right)$ dominates over v^2 . Hence

$$N(v) \propto e^{-\frac{mv^2}{2kT}}$$

Thus $N(v)$ decreases exponentially with increase of v .

When we plot a graph between $n(v)$ and v , the curve starts from the origin ($v = 0, N(v) = 0$) then rises parabolically ($N(v) \propto v^2$) and then falls exponentially.

RMS speed, most probable speed and mean speed

RMS speed

The mean square speed (\bar{v}^2) is given by

$$\bar{v}^2 = \frac{1}{N} \int_0^\infty v^2 N(v) dv$$

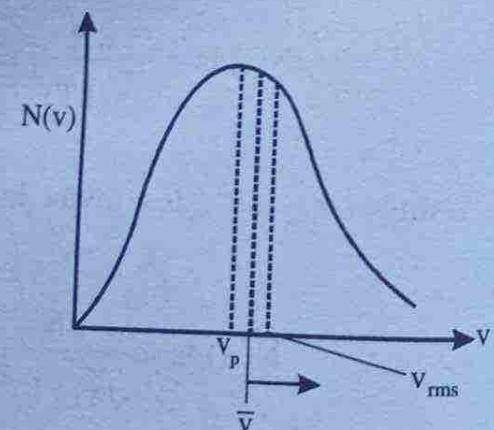


Figure 1.6

$$\bar{v}^2 = \frac{1}{N} \int_0^\infty 4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^4 e^{-\frac{mv^2}{2kT}} dv$$

$$\bar{v}^2 = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_0^\infty v^4 e^{-\frac{mv^2}{2kT}} dv \quad \dots\dots (21)$$

Evaluation of $\int_0^\infty v^4 e^{-\frac{mv^2}{2kT}} dv$

Put $v^2 = x$ then $2v dv = dx$

or $dv = \frac{dx}{2v} = \frac{dx}{2\sqrt{x}}$

$$\begin{aligned} \therefore \int_0^\infty v^4 e^{-\frac{mv^2}{2kT}} dv &= \int_0^\infty x^2 e^{-\frac{mx}{2kT}} \frac{dx}{2\sqrt{x}} \\ &= \frac{1}{2} \int_0^\infty x^{\frac{3}{2}} e^{-\frac{mx}{2kT}} dx \\ &= \frac{1}{2} \left(\frac{3}{2}\right)! \left(\frac{m}{2kT}\right)^{-\frac{3}{2}-1} \\ &= \frac{1}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} \cdot \sqrt{\pi} \cdot \left(\frac{2kT}{m}\right)^{\frac{5}{2}} \\ &= \frac{3}{8} \sqrt{\pi} \cdot \left(\frac{2kT}{m}\right)^{\frac{5}{2}} \end{aligned}$$

Putting this in eqn (21), we get

$$\bar{v}^2 = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \frac{3}{8} \sqrt{\pi} \left(\frac{2kT}{m} \right)^{\frac{5}{2}}$$

$$\bar{v}^2 = \frac{3kT}{m}$$

Taking square root on both sides, we get the rms speed

$$\text{i.e., } v_{\text{rms}} = \sqrt{\bar{v}^2} = \sqrt{\frac{3kT}{m}} \quad \dots\dots (22)$$

Most probable speed (v_p)

Most probable speed is defined as the speed at which the number of molecules is maximum.

i.e., To find the most probable speed, find $\frac{dN(v)}{dv}$, then

$$\text{Put } \frac{dN(v)}{dv} = 0. \text{ Then } v = v_p$$

We have

$$N(v) = 4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$$

$$\frac{dN(v)}{dv} = 4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \left[v^2 e^{-\frac{mv^2}{2kT}} \times -\frac{m}{2kT} 2v + e^{-\frac{mv^2}{2kT}} 2v \right]$$

$$\text{When } \frac{dN(v)}{dv} = 0, v = v_p$$

$$0 = -v_p^2 e^{-\frac{mv_p^2}{2kT}} \frac{mv_p}{kT} + e^{-\frac{mv_p^2}{2kT}} 2v_p$$

$$\text{or } 0 = -\frac{mv_p^3}{kT} + 2v_p$$

$$\text{or } v_p = \sqrt{\frac{2kT}{m}} \quad \dots\dots (23)$$

Mean or average speed (\bar{v})

If there are n_i molecules each having speed v_i , then the mean or average speed (\bar{v}) is defined as

$$\bar{v} = \frac{1}{N} \int_0^\infty N(v)v dv$$

$$\bar{v} = \frac{1}{N} \int_0^\infty 4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^3 e^{-\frac{mv^2}{2kT}} dv$$

$$\bar{v} = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}} dv \quad \dots (24)$$

Evaluation of the Integral $\int_0^\infty v^3 e^{-\frac{mv^2}{2kT}} dv$

put $v^2 = x \therefore 2v dv = dx$

$$\text{or } dv = \frac{dx}{2v} = \frac{dx}{2\sqrt{x}}$$

$$\begin{aligned} \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}} dv &= \int_0^\infty x^{\frac{3}{2}} e^{-\frac{mx}{2kT}} \frac{dx}{2\sqrt{x}} \\ &= \frac{1}{2} \int_0^\infty x e^{-\frac{mx}{2kT}} dx \end{aligned}$$

Using the standard integral

$$= \frac{1}{2} (1)! \left(\frac{m}{2kT} \right)^{-1-1} = \frac{1}{2} \left(\frac{2kT}{m} \right)^2$$

Putting this in eqn 24, we get

$$\begin{aligned} \bar{v} &= 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \cdot \frac{1}{2} \left(\frac{2kT}{m} \right)^2 = \sqrt{\frac{8kT}{\pi m}} \\ \bar{v} &= \sqrt{\frac{8kT}{\pi m}} \quad \dots (25) \end{aligned}$$

From eqn 22, 23 and 25 we can see that

$$v_{\text{rms}} > \bar{v} > v_p$$

(see the figure 1.6)

All equations derived so far (for v_{rms} , v_p and \bar{v}) from statistical considerations are found to be in well agreement with the thermodynamical experimentally verified equations. This is actually the strength of statistical mechanics and its postulates.

Maxwell speed distribution law is more important than Maxwell-Boltzmann energy distribution law. Because all the parameters (v_{rms} , v_p , v_{mean}) predicted can be measured experimentally.

Experimental determination of molecular speeds

The experimental arrangement consists of an oven enclosed in a box provided with hole on one side through which a stream of molecules are escaping. The hole is made small enough so that the distribution of speeds inside the oven is not changed. The beam of molecules is allowed to pass through a slot in a disc attached to an axle rotating at an angular speed ω . At the other end of the axle there is another slotted disc. The slot on the second disc is displaced from the first by an angle θ . In order for a molecule to pass through both slots and strike the detector, it must travel through the length L of the axle in the same time that it takes the axle to rotate by the angle θ .

$$\text{Thus } t = \frac{L}{v} = \frac{\theta}{\omega} \quad \left(\because v = \frac{x}{t} \text{ and } \omega = \frac{\theta}{t} \right)$$

Keeping L and θ fixed, we can vary ω , measuring the number of molecules striking the detector for each different value of ω enables us to measure the Maxwell speed distribution. For a particular ω measure the intensity from the detector.

Increase ω gradually step by step each time measure the intensity from the detector. Plot a graph between v ($v = \frac{L\omega}{\theta}$) along the horizontal axis and intensity along the vertical axis we get a graph perfectly in agreement with Maxwell's speed distribution law. See the experimental arrangement and the graphical result shown below.

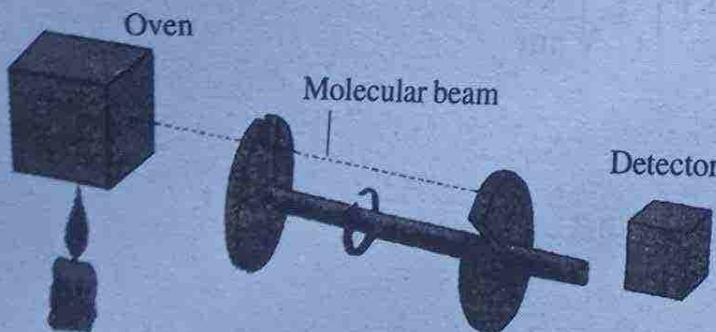


Figure 1.7

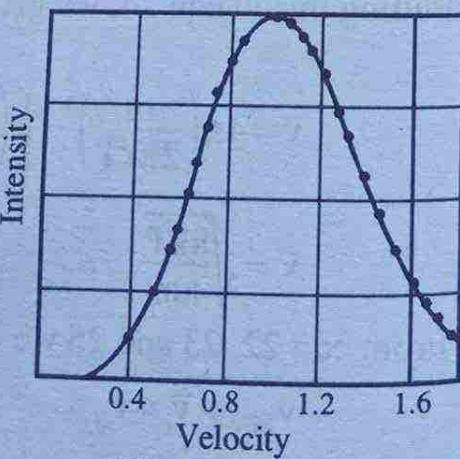


Figure 1.8

Result of measurement of the distribution of atomic speeds in thallium-vapour. The solid line is obtained from the Maxwell speed distribution for an oven temperature of 870 K.

In the experiment what we measure is $N(v)dv$. The range of velocities is dv , determined by the width of the slot. To collect the number of particles with velocity v , we have to make dv , so small. i.e., the slit width is so small. If you make the slit width zero, $dv = 0$ thus $N(v) = 0$.

Quantum statistics

Maxwell-Boltzmann statistics can be applied to classical particles which explained the energy and velocity distribution of the molecules of an ideal gas to a fairly large degree of accuracy. The classical particles are identical and distinguishable. They are distinguishable since the average spacing between the particles is large compared with their de-Broglie wavelength. Moreover while deriving Maxwell-Boltzmann distribution law it has been assumed that all the energy levels are accessible to all the particles of the system. However there are particles which are indistinguishable. They are indistinguishable since the average spacing between the particles is small compared with their de-Broglie wavelengths. (i.e. particles wave functions overlap). Among the several indistinguishable types of particles some of them obey Pauli's exclusion principle and some of them do not. The fermions (half integral spin) are indistinguishable particles which obey Pauli's exclusion principle and certain energy levels are forbidden to these particles. The bosons (integral spin) are also indistinguishable particles which do not obey Pauli's exclusion principle and can accommodate any number of particles in any state. MB statistics failed to explain the phenomena exhibited by these particles. To explain these quantum statistics was developed. The quantum statistics can be classified into two. They are

- (i) Bose-Einstein (BE) statistics
- (ii) Fermi-Dirac statistics.

Bose-Einstein statistics

This statistics was developed by Indian scientist S.N. Bose and later on developed by Albert Einstein. The only difference between the MB statistics and BE statistics is in their distribution functions. It is due to the indistinguishable nature of bosons its distribution function is different from that of classical (MB). The Bose-Einstein distribution function is given by

$$f_{BE}(\varepsilon) = \frac{1}{A_{BE} e^{\beta\varepsilon} - 1} \quad \dots\dots (26)$$

The constant A_{BE} can be evaluated by normalising $f_{BE}(\varepsilon)$. The normalisation depends on the total number of bosons. In the case of photons, where the number is

not conserved, $A_{BE} = 1$. In most of the cases the constant A_{BE} is independent of temperature T or depends so weakly on T.

Fermi-Dirac statistics

This statistics was developed by Enrico Fermi and P.A.M. Dirac hence called Fermi-Dirac statistics shortly called FD statistics. This applies to identical, indistinguishable particles which obey Pauli's exclusion principle (half integral spin particles). These half integral particles are called fermions which are indistinguishable because their wave functions overlap. The only difference between MB statistics and FD statistics is in their distribution function. It is due to the indistinguishable nature and the Pauli's exclusion principle that it obeys FD distribution function is different from that of classical (MB).

The Fermi-Dirac distribution function is given by

$$f_{BE}(\varepsilon) = \frac{1}{A_{FD} e^{\frac{\varepsilon}{kT}} + 1} \quad \dots\dots (27)$$

The term A_{FD} can be evaluated by the theoretical consideration of properties of fermions. It is found that A_{FD} depends strongly on temperature T and evaluated to be

$$A_{FD} = e^{-\frac{\varepsilon_F}{kT}}$$

where ε_F is called the Fermi energy.

Thus

$$f_{FD}(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \varepsilon_F}{kT}} - 1} \quad \dots\dots (28)$$

Equation 28 is called Fermi-Dirac distribution function.

Difference between BE and FD distribution functions

(i) In the BE distribution we have

$$f_{BE}(\varepsilon) = \frac{1}{e^{\frac{\varepsilon}{kT}} - 1} \quad \text{where } A_{BE} = 1 \text{ (assumed)}$$

when the temperature is very small ($T \rightarrow 0$) the exponential factor becomes large for larger energy ε .

So $f_{BE}(\varepsilon) \rightarrow 0$ for $T \rightarrow 0$ and ε large. This means that the probability of occupying higher state at very small temperature ($T \rightarrow 0$) is zero.

When $\varepsilon \rightarrow 0$, T is also small, then

$$f_{BE}(\varepsilon) = \frac{1}{e^{\frac{\varepsilon}{kT}} - 1} = \frac{1}{1-1} = \frac{1}{0} = \infty.$$

This shows that the probability of occupying ground state ($\varepsilon \rightarrow 0$) at very small temperature ($T \rightarrow 0$) is very high ($f_{BE}(\varepsilon) \rightarrow \infty$). This effect is known as Bose-Einstein condensation.

In the case of fermions, we have

$$f_{FD}(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \varepsilon_F}{kT}} + 1}$$

For $\varepsilon > \varepsilon_F$ and $T \rightarrow 0$, then $\varepsilon - \varepsilon_F$ is +ve

$$\therefore f_{FD}(\varepsilon) = \frac{1}{e^{\frac{+ve}{0}} + 1} = \frac{1}{\infty + 1} = \frac{1}{\infty} = 0.$$

This shows that the probability of occupying energy state $\varepsilon > \varepsilon_F$ by the particle is zero at $T \rightarrow 0$. In other words at $T \rightarrow 0$ all particles occupy the energy states $\varepsilon < \varepsilon_F$.

For $\varepsilon < \varepsilon_F$ and $T \rightarrow 0$, then $\varepsilon - \varepsilon_F$ is -ve

$$\therefore f_{FD}(\varepsilon) = \frac{1}{e^{\frac{-ve}{0}} + 1} = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

This shows that the probability of occupying state with energy $\varepsilon < \varepsilon_F$ at very small temperature ($T \rightarrow 0$) is one. The three distribution functions f_{MB} , f_{BE} and f_{FD} are plotted against energy ε are shown below.

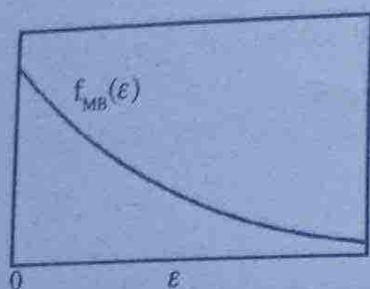


Figure 1.9: The Maxwell-Boltzmann distribution function

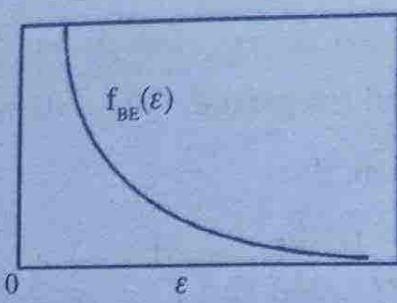


Figure 1.10: The Bose-Einstein distribution function

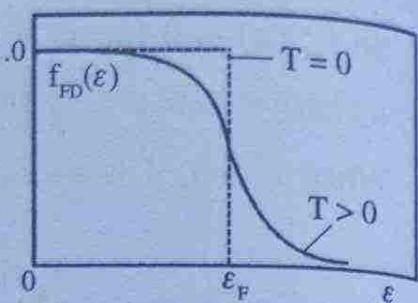


Figure 1.11: The Fermi-Dirac distribution function

The following also may be noted from the graphs.

- All of the distribution functions fall to zero at large values of ϵ . For $\epsilon \gg kT$ the occupation probability is very small.
- When ϵ is very small ($\epsilon \rightarrow 0$)

$f_{MB}(\epsilon)$ is finite

$f_{BE}(\epsilon)$ is infinite

$f_{FD}(\epsilon)$ is one. It can never be greater than one.

- The normalisation constants changes with changing the number of particles of the different distributions. Because normalisation constant depends on the number of particles on the system. The number of particles is determined by integrating the distribution function $f(\epsilon)$ after multiplying it by the density of states $g(\epsilon)d\epsilon$ and volume. In the case of MB distribution when the number of particles increases the intercept rises, thus raising the entire curve. This is as follows

We have $f_{MB}(\epsilon) = A^{-1} e^{-\frac{\epsilon}{kT}}$

To find the intercept put $\epsilon = 0$, then $f_{MB}(\epsilon) = A^{-1}$

But $A^{-1} \propto N$ see equation (19(a)).

In the case of FD distribution, we have

$$f_{FD}(\epsilon) = \frac{1}{e^{\frac{\epsilon - \epsilon_F}{kT}} + 1}$$

For $\varepsilon < \varepsilon_F$, the intercept is 1 at $T = 0$ when the number of particles N increases ε_F increases to accommodate large number of particles as a result the intercept is kept constant at value one.

Fermi energy (ε_F)

To introduce the concept of Fermi energy consider a gas of electrons described by the density function $g(\varepsilon)$ (see equation (12) and $N(\varepsilon)$ is given as

$$N(\varepsilon)d\varepsilon = Vg(\varepsilon)f(\varepsilon)d\varepsilon$$

$$N(\varepsilon)d\varepsilon = V \frac{4\pi\sqrt{2}(2s+1)m^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}d\varepsilon}{e^{\frac{\varepsilon-\varepsilon_F}{kT}} + 1} \quad \dots\dots (29)$$

This equation shows that at $T = 0$, when ε increases $N(\varepsilon)$ increases up to $\varepsilon = \varepsilon_F$ according to $N(\varepsilon) \propto \varepsilon^{1/2}$

When a graph is drawn between $N(\varepsilon)$ and ε , we get almost a parabolic curve governed by $N(\varepsilon) \propto \varepsilon^{1/2}$ up to $\varepsilon = \varepsilon_F$.

The probability of filling the energy state is governed by

$$f(\varepsilon) = \frac{1}{e^{\frac{\varepsilon-\varepsilon_F}{kT}} + 1}$$

$$f(\varepsilon) = 1 \quad \text{for } \varepsilon < \varepsilon_F \text{ at } T = 0K$$

This shows that up to $\varepsilon = \varepsilon_F$, all energy levels are filled.

When $\varepsilon > \varepsilon_F$ at $T = 0K$

$$f(\varepsilon) = 0$$

This means that $\varepsilon > \varepsilon_F$ at 0K the levels are completely empty. This is shown in figure 1.12.

The above discussion enables us to define Fermi energy ε_F .

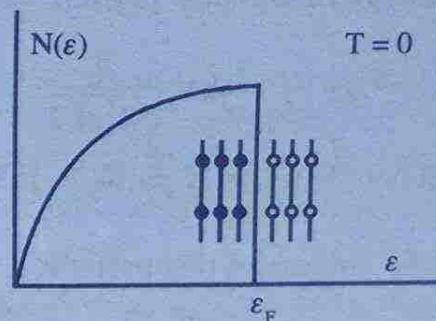


Figure 1.12: The occupation probability of electrons at $T = 0K$

The Fermi energy is the energy value upto which all the energy states are filled at 0K and above which all energy states are empty.

When $T > 0$, at $\epsilon = \epsilon_F$, we have

$$f_{FD}(\epsilon) = \frac{1}{e^{\frac{\epsilon - \epsilon_F}{kT}} + 1} = \frac{1}{e^0 + 1} = \frac{1}{2}$$

Thus the Fermi energy ϵ_F at $T > 0\text{K}$ is that energy level in which 50% of the levels are occupied and 50% are empty. This was shown in figure 1.12.

When we draw a graph between $N(\epsilon)$ and ϵ at $T > 0\text{K}$, we get graph as shown in figure 1.13.

Limits of classical statistics

For particles to be treated as classical it should be possible to neglect its quantum behaviour. This is possible when the de Broglie wavelength (λ) is much smaller than the average separation between the particles d . i.e. for a classical particle the only criterion to be satisfied is

$$\lambda \ll d \quad \text{or} \quad \frac{\lambda}{d} \ll 1 \quad \dots\dots (30)$$

We have $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m\epsilon}}$, $\epsilon = \frac{p^2}{2m}$

Energy of classical particle is of the order of kT . i.e. $\epsilon \approx kT$

$$\lambda = \frac{h}{\sqrt{2mkT}}$$

When there are N particles in volume V .

$$\text{The volume of one particle} = \frac{V}{N}$$

i.e. $\frac{4}{3}\pi r^3 = \frac{V}{N}$, where r is the radius of the particle.

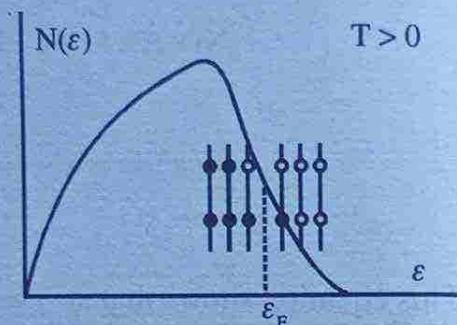


Figure 1.13: The occupation probability of electrons at $T > 0\text{K}$

$$\therefore r^3 = \frac{3}{4\pi} \left(\frac{V}{N} \right) \approx \frac{1}{4} \frac{V}{N}$$

$$r \approx \left(\frac{1}{4} \right)^{\frac{1}{3}} \left(\frac{V}{N} \right)^{\frac{1}{3}}$$

\therefore The separation between the particles

$$d = 2r = 2 \left(\frac{1}{4} \right)^{\frac{1}{3}} \left(\frac{V}{N} \right)^{\frac{1}{3}}$$

$$\text{or } d \approx \left(\frac{V}{N} \right)^{\frac{1}{3}}$$

Putting the value of λ and d in equation (30)

$$\text{we get } \frac{h}{\sqrt{2mkT}} \left(\frac{N}{V} \right)^{\frac{1}{3}} \ll 1 \quad \dots\dots (31)$$

This is the condition to be satisfied for treating the particle as classical. Recall our expression for normal constant A^{-1} from Maxwell-Boltzmann distribution.

$$A^{-1} = \frac{Nh^3}{V(2s+1)(2\pi mkT)^{\frac{3}{2}}} \quad (\text{see eqn 19(a)})$$

From equation 31, we have (cubing it)

$$\frac{N}{V} \frac{h^3}{(2mkT)^{\frac{3}{2}}} \ll 1$$

$$\text{This gives us } A^{-1} \ll 1 \quad \dots\dots (27)$$

This says that the normalisation constant of the Maxwell-Boltzmann distribution must be very small for the validity of the condition for classical particles. In other words the number of occupied states in the gas is much smaller than the number of available states.

Note: A rigorous mathematical derivation shows that the de-Broglie wavelength is

$$\lambda = \frac{h}{\sqrt{2\pi mkT}}, \text{ using this we get the exact result.}$$

Example 13

Check whether the Maxwell-Boltzmann statistics can be applied to the following

- A nitrogen gas at standard temperature ($T = 293\text{ K}$) and pressure $1.0 \times 10^5\text{ Nm}^{-2}$
- Liquid water at room temperature 27°C .

Solution

$$(i) P = 1.0 \times 10^5\text{ Nm}^{-2}, T = 293\text{K}, m_{N_2} = 28\text{u} \quad 1\text{u} = 1.66 \times 10^{-27}\text{ kg}$$

Using $PV = NkT$, we get

$$\frac{N}{V} = \frac{P}{kT} = \frac{1 \times 10^5}{1.38 \times 10^{-23} \times 293} = 2.47 \times 10^{25}$$

For Maxwell-Boltzmann statistics to be applied $\frac{h}{\sqrt{2mkT}} \left(\frac{N}{V} \right)^{1/3}$ must be very much less than one.

$$\frac{\lambda}{d} = \frac{h}{\sqrt{2mkT}} \left(\frac{N}{V} \right)^{1/3} = \frac{6.64 \times 10^{-34} \times (2.47 \times 10^{25})^{1/3}}{\sqrt{2 \times 28 \times 1.66 \times 10^{-27} \times 1.38 \times 10^{-23} \times 293}}$$

$$\frac{\lambda}{d} = \frac{6.64 \times 10^{-34} \times 2.91 \times 10^8}{193.87 \times 10^{-25}} = \frac{6.64 \times 2.91 \times 10^{-26}}{193.87 \times 10^{-25}}$$

$$\frac{\lambda}{d} = \frac{6.64 \times 0.291}{193.87} = 0.0099 \approx 0.01$$

Since $\frac{\lambda}{d} \ll 1$, it is possible to apply MB statistics.

$$(ii) \text{ For water } \frac{N}{V} = \frac{N}{m/d} = \frac{Nd}{m}$$

$d = 10^3\text{ kgm}^{-3}$, $m = 18\text{u} = 18 \times 1.66 \times 10^{-27}\text{ kg}$ and $N = 1$ (one molecule)

$$\therefore \frac{N}{V} = \frac{10^3}{18 \times 1.66 \times 10^{-27}} = 3.25 \times 10^{28}$$

$$\therefore \frac{\lambda}{d} = \frac{h}{\sqrt{2mkT}} \left(\frac{N}{V} \right)^{1/3}$$

$$\frac{\lambda}{d} = \frac{6.64 \times 10^{-34} \times (3.35 \times 10^{28})^{1/3}}{(2 \times 18 \times 1.66 \times 10^{-27} \times 1.38 \times 10^{-23} \times 300)^{1/2}}$$

$$\frac{\lambda}{d} = \frac{6.64 \times 10^{-34} \times 3.22 \times 10}{157.3 \times 10^{-25}}$$

$$\frac{\lambda}{d} = \frac{21.38 \times 10^{-25}}{157.3 \times 10^{-25}} = \frac{21.38}{157.3} = 0.14$$

Since $\frac{\lambda}{d}$ is not very much than one, so MB statistics cannot be applicable to liquid water at 27°C.

Example 14

For what temperatures are the atoms in an ideal gas at pressure P quantum mechanical. $P = 1.0 \times 10^5 \text{ Nm}^{-2}$. Take H₂ gas.

Solution

We have $\frac{h}{\sqrt{2mkT}} \left(\frac{N}{V} \right)^{\frac{1}{3}} \gg 1$ squaring on both sides, we get

$$\frac{h^2}{2mkT} \left(\frac{N}{V} \right)^{\frac{2}{3}} \gg 1$$

$$\text{or } T \ll \frac{h^2}{2mk} \left(\frac{N}{V} \right)^{\frac{2}{3}}$$

$$\text{Using } PV = NkT \text{ gives } \frac{N}{V} = \frac{P}{kT}$$

$$T \ll \frac{h^2}{2mk} \left(\frac{P}{kT} \right)^{\frac{2}{3}}$$

$$T^{\frac{5}{3}} \ll \frac{h^2 P^{\frac{2}{3}}}{2mk^{\frac{5}{3}}}$$

or $T \ll \frac{h^{\frac{6}{5}} P^{\frac{2}{5}}}{(2m)^{\frac{3}{5}} k}$

Substituting the values of h, P, m and k

$$T \ll \frac{(6.64 \times 10^{-34})^{\frac{6}{5}} (10^5)^{\frac{2}{5}}}{(2 \times 2 \times 1.66 \times 10^{-27})^{\frac{3}{5}} \times 1.38 \times 10^{-23}}$$

$$T \ll \frac{(66.4)^{\frac{6}{5}} \times 10^{-42} \times 100}{(4 \times 0.0166) \times 10^{-15} \times 1.38 \times 10^{-23}}$$

$$T \ll \frac{(66.4)^{\frac{6}{5}} \times 10^{-40}}{(4 \times 0.166)^{\frac{3}{5}} \times 1.38 \times 10^{-38}}$$

$$T \ll \frac{(66.4)^{\frac{6}{5}} \times 10^{-2}}{(4 \times 0.166)^{\frac{3}{5}} \times 1.38}$$

$$T \ll \frac{153.7 \times 10^{-2}}{0.782 \times 1.38} = \frac{1.537}{0.782 \times 1.38}$$

$$T \ll 1.42\text{K}$$

This shows that only when the temperature is very much below 1.42K, hydrogen gas can be treated as quantum mechanical. i.e. at ordinary temperatures it is a classical system.

Applications of Bose-Einstein statistics

Black body radiation

The electromagnetic radiation trapped in a cavity and in thermal equilibrium with the walls of the cavity are termed as black body radiation. In thermal equilibrium condition, the black body radiation can be considered as the photon gas. Photons have spin 1, so they are bosons and obey Bose-Einstein statistics.

The number of photon having energy between ε and $\varepsilon + d\varepsilon$, according to Bose-Einstein distribution is given by

$$N(\varepsilon)d\varepsilon = Vg(\varepsilon)f_{BE}(\varepsilon)d\varepsilon$$

The density of state

$$g(\varepsilon) = \frac{8\pi\varepsilon^2}{h^3c^3} \text{ (see eqn 14)}$$

and the distribution function

$$f_{BE}(\varepsilon) = \frac{1}{A_{BE}e^{\frac{\varepsilon}{kT}} - 1}$$

In the case of photons, the normalisation constant has no relevance since photon number is not conserved in nature. So we set $A_{BE} = 1$.

Thus $N(\varepsilon)d\varepsilon = \frac{V8\pi\varepsilon^2}{h^3c^3} \cdot \frac{d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1}$

since each photon has energy ε , the energy carried by $N(\varepsilon)$ photon is

$$\varepsilon N(\varepsilon)d\varepsilon = \frac{V8\pi\varepsilon^3}{h^3c^3} \frac{d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1}$$

or

$$\frac{\varepsilon N(\varepsilon)d\varepsilon}{V} = \frac{8\pi\varepsilon^3}{h^3c^3} \frac{d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1}$$

since $\frac{\text{Total energy}}{\text{Volume}} = \text{Energy density } u(\varepsilon)$

$$\therefore u(\varepsilon)d\varepsilon = \frac{8\pi\varepsilon^3}{h^3c^3} \frac{d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1} \quad \dots \quad (32)$$

From this the total energy density over all photon energies can be calculated by integrating the above equation.

i.e. $u = \int_0^\infty u(\varepsilon)d\varepsilon = \frac{8\pi}{h^3c^3} \int_0^\infty \frac{\varepsilon^3 d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1} \quad \dots \quad (33)$

put $\frac{\varepsilon}{kT} = x$

and $d\varepsilon = kTdx$ in the above integral,

$$\int_0^{\infty} \frac{(kT)^3 x^3 (kT) dx}{e^x - 1} = (kT)^4 \int_0^{\infty} \frac{x^3 dx}{e^x - 1}$$

The integral can be easily calculated to be $\frac{\pi^4}{15}$ (see example 15)

$$u = \frac{8\pi^5 (kT)^4}{15h^3 c^3} = \frac{8\pi^5 k^4 T^4}{15h^3 c^3} \quad \dots \dots (34)$$

From this we can calculate the radiant intensity R which is the radiation energy emitted per unit area per second.

$$\text{Radiant intensity, } R = \frac{c}{4} u.$$

$$R = \frac{c}{4} \frac{8\pi^5 k^4}{15h^3 c^3} T^4$$

$$R = \frac{2\pi^5 k^4}{15h^3 c^2} T^4 = AT^4$$

$$\text{where } A = \frac{2\pi^5 k^4}{15h^3 c^2}$$

Substituting the values of k , h and c we get $A = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$.

This is the famous Stefan's constant denoted by σ

$$R = \sigma T^4 \quad \dots \dots (35)$$

This is nothing but Stefan's law.

The above discussion shows that Bose-Einstein's statistics is in perfect agreement with Stefan's law.

From equation 32, we can easily arrive at Planck's radiation law.

Put $\epsilon = hv$ in equation 32, we get

$$u(v)dv = \frac{8\pi(hv)^3}{h^3 c^3} \frac{hdv}{e^{\frac{hv}{kT}} - 1}$$

$$u(v)dv = \frac{8\pi h v^3}{c^3} \frac{dv}{e^{\frac{hv}{kT}} - 1} \quad \dots \dots (36)$$

This is the famous Planck's radiation law for black body radiation.

Planck's law in terms of wavelength

We have $u(v)dv = \frac{8\pi h v^3}{c^3} \frac{dv}{e^{\frac{hv}{kT}} - 1}$

Using $v = \frac{c}{\lambda}$ and $dv = -\frac{c}{\lambda^2} d\lambda$

$$\therefore u(\lambda)d\lambda = \frac{8\pi h}{c^3} \cdot \frac{c^3}{\lambda^3} \frac{c}{\lambda^2} \frac{d\lambda}{e^{\frac{hc}{\lambda kT}} - 1}$$

$$u(\lambda)d\lambda = \frac{8\pi h c \lambda^{-5}}{e^{\frac{hc}{\lambda kT}} - 1} d\lambda \quad \dots \dots (37)$$

This is the Planck's radiation law in terms of wavelength.

The Planck's radiation law which is in perfect agreement with experimental results. Now we proved that Planck's radiation law can also be derived using Bose-Einstein statistics. It may also be remembered that Max-Planck derived his radiation law two decades before the development of Bose-Einstein statistics.

Example 15

Show that $\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$

Solution

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \int_0^\infty x^3 (e^x - 1)^{-1} dx = \int_0^\infty x^3 e^{-x} (1 - e^{-x})^{-1} dx$$

since $e^{-x} < 1$, we can use Binomial expansion

$$= \int_0^\infty x^3 e^{-x} (1 + e^{-x} + e^{-2x} + e^{-3x} + \dots) dx$$

$$= \int_0^{\infty} x^3 (e^{-x} + e^{-2x} + e^{-3x} + \dots) dx$$

$$= \int_0^{\infty} x^3 \sum_{m=1}^{\infty} e^{-mx} dx$$

$$= \sum_{m=1}^{\infty} \int_0^{\infty} x^3 e^{-mx} dx$$

Using the standard integral $\int_0^{\infty} x^n e^{-ax} dx = n! (a)^{-n-1}$

$$\begin{aligned} \therefore \int_0^{\infty} \frac{x^3}{1-e^x} dx &= \sum_{m=1}^{\infty} 3! (m)^{-3-1} = 6 \sum_{m=1}^{\infty} \frac{1}{m^4} \\ &= 6 \cdot \frac{\pi^4}{90} \quad \left(\because \sum_{m=1}^{\infty} \frac{1}{m^4} = \frac{\pi^4}{90} \right) \\ &= \frac{\pi^4}{15} \end{aligned}$$

Example 16

Calculate the number of photons per cm^3 in a volume filled with radiation at 300K given $\int_0^{\infty} \frac{x^2}{e^x - 1} dx = 2.404$.

Solution

The number of photons having frequencies between ν and $\nu + d\nu$ in volume V is given by

$$n(\nu) d\nu = \frac{8\pi V}{c^3} \frac{\nu^2 d\nu}{\left(e^{\frac{h\nu}{kT}} - 1 \right)} \quad (\text{see eqn 32, where } \varepsilon = h\nu)$$

\therefore The total number of photons per unit volume and with all possible frequencies (0 to ∞).

$$N = \frac{1}{V} \int_0^{\infty} n(v) dv = \frac{8\pi}{c^3} \int_0^{\infty} \frac{v^2 dv}{\left(e^{\frac{hv}{kT}} - 1 \right)}$$

put $\frac{hv}{kT} = x$ and $\frac{hdv}{kT} = dx$

$$\therefore N = \frac{8\pi}{c^3} \int_0^{\infty} \left(\frac{kT}{h} \right)^3 \frac{x^2 dx}{e^x - 1} = \frac{8\pi}{c^3} \left(\frac{kT}{h} \right)^3 \int_0^{\infty} \frac{x^2 dx}{e^x - 1}$$

or $N = \frac{8\pi (kT)^3}{c^3 h^3} \times 2.404$

$$= \frac{19.23 \times 3.14 \times (1.38 \times 10^{-16})^3 (300)^3}{(3 \times 10^{10})^3 \times (6.62 \times 10^{-34})^3}$$

$$= 5.4 \times 10^8 \text{ cm}^{-3}.$$

Example 17

Sunlight arrives at the earth at the rate of about 1.4 kW m^{-2} . The average radius of the earth's orbit is $1.5 \times 10^{11} \text{ m}$ and the radius of the sun is $7 \times 10^8 \text{ m}$. Calculate the surface temperature of the sun.

Solution

The solar energy received per second per unit area $= 1.4 \times 10^3 \text{ W m}^{-2}$

\therefore The total solar energy received per second by area of a sphere whose radius r_e is that of earth's orbital radius is $4\pi r_e^2$.

$$= 1.4 \times 10^3 \times 4\pi r_e^2$$

$$= 1.4 \times 10^3 \times 4 \times 3.14 \times 1.5 \times 10^{11}$$

$$= 3.96 \times 10^{26} \text{ W} \quad \dots\dots (1)$$

This is equal to the total energy radiated by the sun per second.

According to Stefan's law, the energy radiated by a perfect black body per second per unit area

$$R = \sigma T^4$$

\therefore The total energy radiated by the sun per second

$$\begin{aligned}
 &= 4\pi r_s^2 \sigma T^4 \\
 &= 4\pi (7 \times 10^8)^2 \times 5.67 \times 10^{-8} T^4 \\
 &= 3489.55 \times 10^8 T^4
 \end{aligned} \quad \dots\dots (2)$$

Equating eqns 1 and 2, we get

$$3489.55 \times 10^8 T^4 = 3.96 \times 10^{26}$$

$$\text{or } T^4 = \frac{3.96 \times 10^{26}}{3489.55 \times 10^8} = 1.1348 \times 10^{15}$$

$$T^4 = 1134.8 \times 10^{12}$$

$$T = (1134.8 \times 10^{12})^{\frac{1}{4}} = 5.8 \times 10^3 \text{ K.}$$

Example 18

What is the average energy of photons in eV present in 1 cm³ of radiation at 727°C.

Solution

We have, the total energy per unit volume is

$$u = \frac{8\pi^5 k^4 T^4}{15 c^3 h^3} \quad (\text{see eqn 34}) \quad \dots\dots (1)$$

Total number of photons per unit volume is

$$N = \frac{8\pi k^3 T^3}{c^3 h^3} \times 2.404 \quad (\text{see example 16}) \quad \dots\dots (2)$$

\therefore Average energy of photons

$$\begin{aligned}
 \bar{u} &= \frac{u}{N} = \frac{\pi^4 k T}{15 \times 2.404} \\
 &= \frac{(3.14)^4 \times 1.38 \times 10^{-16} \times 1000}{15 \times 2.404} \\
 &= 3.72 \times 10^{-13} \text{ ergs.}
 \end{aligned}$$

$$\bar{u} = \frac{3.72 \times 10^{-13}}{1.6 \times 10^{-12}} \text{ eV} = 0.2325 \text{ eV.}$$

Example 19

A black body is radiating at a temperature of 2.50×10^3 K. a) What is the total energy density of radiation. b) What fraction of the energy is emitted in the interval between 1.00 and 1.05 eV.

Solution

a) $T = 2.50 \times 10^3$ K.

Total energy density of radiation is

$$u = \frac{8\pi^5 k^4}{15h^3 c^3} T^4$$

$$u = \frac{8 \times (3.14)^5 \times (1.38 \times 10^{-23})^4 \times (2.5 \times 10^3)^4}{15 \times (6.64 \times 10^{-34})^3 (3 \times 10^8)^3}$$

$$u = \frac{8 \times (3.14)^5 \times (1.38)^4 \times (2.5)^4 \times 10^{-80}}{15 \times (6.64)^3 \times 3^3 \times 10^{-78}}$$

$$u = \frac{8 \times (3.14)^5 \times (1.38)^4 \times (2.5)^4 \times 10^{-2}}{15 \times (6.64)^3 \times 3^3}$$

$$u = \frac{3459.5}{118.57 \times 10^3} = 2.91 \times 10^{-2}$$

$$u = 0.0291 \text{ J m}^{-3}$$

$$u = \frac{0.0291}{1.6 \times 10^{-19}} \text{ eV m}^{-3}$$

$$u = 1.82 \times 10^{17} \text{ eV m}^{-3}$$

b) $T = 2.5 \times 10^3$ K, $\epsilon = 1.00$ eV, $d\epsilon = 0.05$ eV

The energy emitted in the interval

$$u(\epsilon)d\epsilon = \frac{8\pi}{h^3 c^3} \frac{\epsilon^3}{e^{\frac{\epsilon}{kT}} - 1} d\epsilon$$

$$kT = 8.625 \times 10^{-5} \times 2.5 \times 10^3 \text{ eV} = 0.216 \text{ eV}$$

$$u(\varepsilon)d\varepsilon = \frac{8 \times 3.14 \times (1\text{eV})^3 \times 0.05\text{eV}}{(1240 \text{ eVnm})^3 \left(e^{\frac{1}{0.216}} - 1 \right)}$$

$$\begin{aligned} u(\varepsilon)d\varepsilon &= \frac{25.12}{1.24^3 (\text{nm} \times 10^{-3})^3} \frac{\text{eV}}{101.48} \\ &= \frac{25.12}{1.24^3 (10^{-6})^3 \text{m}^3} \frac{\text{eV}}{101.48} \\ &= 6.49 \times 10^{15} \text{eVm}^{-3} \end{aligned}$$

\therefore The fraction, $\frac{u(\varepsilon)d\varepsilon}{u} = \frac{6.49 \times 10^{15}}{1.82 \times 10^{17}} = 0.036$

Applications of Fermi-Dirac statistics

The most important application of the Fermi-Dirac statistics is in predicting the behaviour of free electrons inside metals. These electrons are responsible for the high conductivities of metals like copper, silver, gold etc. These electrons freely move about inside the metal, colliding against the fixed ions. Thus they form a sort of gas known as an electron gas. Since the electrons are fermions they obey Fermi-Dirac statistics.

According to Fermi-Dirac statistics, the number of electrons having energy between ε and $\varepsilon + d\varepsilon$ is given by

$$N(\varepsilon)d\varepsilon = Vg(\varepsilon)f_{FD}(\varepsilon)d\varepsilon$$

$$\text{The density of states } g(\varepsilon) = \frac{8\pi\sqrt{2}m^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}}{h^3} \text{ (see eqn 12 where } s = \frac{1}{2} \text{)}$$

$$\text{The distribution function } f_{FD}(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \varepsilon_F}{kT}} + 1}$$

$$\therefore N(\varepsilon)d\varepsilon = V \frac{8\sqrt{2}\pi m^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}}{h^3} \frac{d\varepsilon}{e^{\frac{\varepsilon - \varepsilon_F}{kT}} + 1} \quad \dots\dots (38)$$

This is known as Fermi-Dirac distribution law of electrons.

Expression for Fermi energy (ϵ_F)

The Fermi energy is defined at 0K. At T = 0K, the distribution function

$$f_{FD}(\epsilon) = \begin{cases} 1 & \text{for } \epsilon < \epsilon_F \\ 0 & \text{for } \epsilon > \epsilon_F \end{cases}$$

Integrating equation 38, we get the total number of particles.

$$\text{i.e., } N = \int_0^{\epsilon_F} \frac{V8\sqrt{2}\pi m^{\frac{3}{2}}\epsilon^{\frac{1}{2}}}{h^3} d\epsilon$$

At T = 0K, the minimum energy of the particle is 0 and its maximum value is ϵ_F

$$N = \frac{V8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} \int_0^{\epsilon_F} \epsilon^{\frac{1}{2}} d\epsilon$$

$$N = \frac{V8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} \left[\frac{\epsilon^{\frac{3}{2}}}{\frac{3}{2}} \right]_0^{\epsilon_F}$$

$$N = \frac{16\sqrt{2}Vm^{\frac{3}{2}}}{3h^3} \epsilon_F^{\frac{3}{2}} \quad \dots\dots (39)$$

$$\text{or } \epsilon_F^{\frac{3}{2}} = \frac{3Nh^3}{16\sqrt{2}Vm^{\frac{3}{2}}} = \frac{h^3}{2^{\frac{3}{2}}m^{\frac{3}{2}}} \left(\frac{3N}{8\pi V} \right)$$

$$\text{or } \epsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{\frac{2}{3}} \quad \dots\dots (40)$$

This is the expression for Fermi energy of electron system

Average electron energy at absolute zero (0K)

To calculate the average energy at 0K, first all we have to calculate the total energy E possessed by the electrons at 0K.

$$\text{Total energy at 0K, } E = \int_0^{\epsilon_F} \epsilon N(\epsilon) d\epsilon$$

Substituting for $N(\epsilon)d\epsilon$ from equation 38 by putting $T = 0K$, we get

$$N(\epsilon)d\epsilon = \frac{V8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} d\epsilon$$

$$E = \int_0^{\epsilon_F} \frac{\epsilon V8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} d\epsilon$$

$$E = \frac{V8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} \int_0^{\epsilon_F} \epsilon^{\frac{3}{2}} d\epsilon$$

$$E = \frac{V8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} \left[\frac{\epsilon^{\frac{5}{2}}}{5/2} \right]_0^{\epsilon_F}$$

$$E = \frac{16\sqrt{2} V\pi m^{\frac{3}{2}}}{5 h^3} \epsilon_F^{\frac{5}{2}} \quad \dots\dots (41)$$

Eq 41
Eq 39 gives

$$\frac{E}{N} = \frac{3}{5} \epsilon_F$$

$$\frac{E}{N} = \frac{\text{Total energy}}{\text{Total number}} = \bar{\epsilon}_0, \text{ average energy per electron.}$$

Thus $\bar{\epsilon}_0 = \frac{3}{5} \epsilon_F.$

Example 20

In copper there is one free electron per atom. Calculate the Fermi energy of free electrons in copper.

Given : Atomic weight of copper 63.5 g / mole

Density of copper = $8.94 \times 10^3 \text{ g cm}^{-3}$

Avagadro number = $6.02 \times 10^{23} \text{ atoms /mole}$

Solution

Number density of free electrons in copper

= Number of atoms per cm^3 .

$$\text{i.e., } \frac{N}{V} = \frac{6.02 \times 10^{23}}{63.5} \times 8.94 = 8.48 \times 10^{22} \text{ electrons cm}^{-3}$$

$$\frac{N}{V} = 8.48 \times 10^{28} \text{ electrons m}^{-3}.$$

$$\text{Using } \epsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{\frac{2}{3}}$$

$$\epsilon_F = \frac{(6.62 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}} \left(\frac{3 \times 8.48 \times 10^{28}}{8 \times 3.14} \right)^{\frac{2}{3}}$$

$$= 1.13 \times 10^{-18} \text{ J} = \frac{1.13 \times 10^{-18}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 7.06 \text{ eV.}$$

Example 21

Fermi energy of conduction electrons in silver is 5.48 eV. Calculate the number of such electrons per m^3 .

Solution

$$\text{We have } \epsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{\frac{2}{3}}$$

$$\text{or } \epsilon_F^{\frac{3}{2}} = \frac{h^3}{(2m)^{\frac{3}{2}}} \frac{3N}{8\pi V}$$

$$\therefore \frac{N}{V} = \frac{8\pi}{3h^3} (2m)^{\frac{3}{2}} \epsilon_F^{\frac{3}{2}}$$

$$= \frac{8 \times 3.14 \times (2 \times 9.1 \times 10^{-31})^{\frac{3}{2}} \times (5.48 \times 1.6 \times 10^{-19})^{\frac{3}{2}}}{3(6.62 \times 10^{-34})^3}$$

$$\text{or } \frac{N}{V} = 5.9 \times 10^{28} \text{ m}^{-3}.$$

Example 22

A certain metal has Fermi energy 3.00 eV. Find the number of electrons per unit volume with energy between 5.00 eV and 5.10 eV for T = 295 K.

Solution

$$\frac{N(\varepsilon)d\varepsilon}{V} = \frac{8\pi\sqrt{2}m^{\frac{3}{2}}}{h^3}\varepsilon^{\frac{1}{2}} \frac{d\varepsilon}{e^{\frac{\varepsilon-\varepsilon_F}{kT}} + 1}$$

$$\frac{\varepsilon - \varepsilon_F}{kT} = \frac{5 - 3}{8.625 \times 10^{-5} \times 295} = 80,$$

$$\therefore e^{\frac{\varepsilon - \varepsilon_F}{kT}} = e^{80} = 5.54 \times 10^{34} \text{ and } d\varepsilon = 5.10 - 5.00 \text{ eV} = 0.10 \text{ eV}$$

$$\begin{aligned} \frac{N(\varepsilon)d\varepsilon}{V} &= \frac{8 \times 3.14 \times \sqrt{2} \times (9.1 \times 10^{-31})^{\frac{3}{2}} (5 \times 1.6 \times 10^{-19})^{\frac{1}{2}} \times 0.1 \times 1.6 \times 10^{-19}}{(6.64 \times 10^{-34})^3 \times 5.54 \times 10^{34}} \\ &= 8.81 \times 10^{-10} \text{ m}^{-3}. \end{aligned}$$

Fermi-Dirac statistics has several applications. Some of them are

- (i) to find out the radius and limiting mass of white dwarf stars
- (ii) to find out the relation between mass and radius of neutron stars
- (iii) to find out the heat capacities of dilute solutions and also that of metals.

IMPORTANT FORMULAE

1. Probability of energy, $p(\epsilon) = \frac{\sum N_i W_i}{N \sum_i W_i}$ where i runs over all macrostates
2. Multiplicity of macrostate, $W = \frac{N!}{\prod_{i=0}^N N_i!}$
3. When N particles share Q integral units of energy, the total number of microstates (multiplicity), $W_{\text{total}} = \frac{(N+Q-1)!}{Q!(N-1)!}$
4. When there are g_i states and N_i number of classical particles, the number of microstates possible $W = g_i^{N_i}$
5. When there are g_i states and N_i number of bosons, the number of microstates is $W = \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$
6. When there are g_i states and N_i number of fermions, the number of microstates $W = \frac{g_i!}{N_i!(g_i - N_i)!}$
7. The number of particles (N_n) in the system with energy ϵ_n and probability $f(\epsilon_n)$ is $N_n = d_n f(\epsilon_n)$, where d_n is the degeneracy.
Total number of particles $N_n = \sum_n N_n = \sum_n d_n f(\epsilon_n)$ where n runs over all discrete energy states.
8. The total number of states in the interval $d\epsilon$
 $dN = N(\epsilon)d\epsilon = Vg(\epsilon)f(\epsilon)d\epsilon$
where $g(\epsilon)$ is the density of states.

$$N = \int_0^\infty N(\epsilon)d\epsilon = \int_0^\infty Vg(\epsilon)f(\epsilon)d\epsilon$$

9. Density of states in a gas of particles

$$g(\varepsilon) = \frac{4\pi\sqrt{2}(2s+1)m^{3/2}\varepsilon^{1/2}}{h^3}$$

10. Density of states in terms of momentum

$$g(\varepsilon) = \frac{4\pi(2s+1)p^2 dp}{h^3} - \ln 3D$$

11. Density of states in a gas of photons

$$g(\varepsilon) = \frac{8\pi\varepsilon^2}{h^3 c^3}$$

12. Maxwell-Boltzmann distribution function

$$f_{MB}(\varepsilon) = A^{-1} e^{-\beta\varepsilon}$$

13. Maxwell-Boltzmann energy distribution law

$$N(\varepsilon)d\varepsilon = \frac{2N}{\sqrt{\pi(kT)^{3/2}}} \varepsilon^{1/2} e^{-\frac{\varepsilon}{kT}}$$

14. Maxwell-Boltzmann speed distribution law

$$N(v)dv = N \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv$$

15. Expressions for rms speed, most probable speed and average speed

$$(i) v_{rms} = \sqrt{\frac{3kT}{m}}$$

$$(ii) v_p = \sqrt{\frac{2kT}{m}}$$

$$(iii) \bar{v} = \sqrt{\frac{8kT}{m}}$$

$$v_{rms} > \bar{v} > v_p$$

16. Bose-Einstein distribution function

$$f_{BE}(\varepsilon) = \frac{1}{A_{BE} e^{\frac{\varepsilon}{kT}} - 1}$$

$$A_{BE} = 1 \text{ for photons.}$$

17. Fermi-Dirac distribution function

$$f_{FD}(\epsilon) = \frac{1}{e^{\frac{\epsilon - \epsilon_F}{kT}} + 1}$$

(i) $f_{FD}(\epsilon) = 1$ for $\epsilon < \epsilon_F$ at $T = 0K$

$= 0$ for $\epsilon > \epsilon_F$ at $T = 0K$

(ii) $f_{FD}(\epsilon) = \frac{1}{2}$ for $\epsilon = \epsilon_F$ at $T > 0K$.

18. Expression for Fermi energy of electron system

$$\epsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

19. Expression for average electron energy at absolute zero

$$\bar{\epsilon}_0 = \frac{3}{5} \epsilon_F$$

20. Condition to be satisfied to treat particle as classical

$$\frac{\lambda}{d} \ll 1, \quad \lambda = \frac{h}{\sqrt{2mkT}} \text{ and } d \approx \left(\frac{N}{V} \right)^{1/3}$$

$$\text{or} \quad \frac{h}{\sqrt{2mkT}} \left(\frac{N}{V} \right)^{1/3} \ll 1$$

In terms of temperature:

$$T \gg \frac{h^2}{2mk} \left(\frac{N}{V} \right)^{2/3}$$

In terms of pressure:

$$P \ll \frac{(2m)^{3/2} (kT)^{5/2}}{h^3}.$$

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in two or three sentences)

Short answer type questions

1. What is statistical mechanics?
2. Write down three phenomena which essentially require statistical mechanics to explain it.
3. What is meant by statistical analysis?
4. What is meant by macroscopic property of a system?
5. What is meant by microscopic property of a system?
6. Define the macrostate of a system.
7. Define the microstate of a system.
8. Four distinguishable particles are distributed in two states. Find the total number of microstates.
9. Four indistinguishable particles obeying Pauli's exclusion principle are distributed in 5 quantum states. Find the total number of microstates possible.
10. A gas has 3 particles. How these particles can be arranged in 4 quantum states according to Bose-Einstein distribution?
11. What is the physical implication of increasing multiplicity?
12. Write down the statement of the implicit postulate in statistical analysis.
13. Write down an expression for probability of occurrence of particles with energy ϵ and explain the symbols.
14. Distinguish between classical and quantum particles.
15. Write down an expression for calculating the multiplicity of each microstate in the macrostate and explain the symbols.
16. N particles share Q integral units of energy. How will you calculate the multiplicity of the system?
17. Show graphically how does the classical probability $p(\epsilon)$ vary with energy ϵ .
18. Write down the three probability distribution functions and explain the symbols.
19. Define density of states.
20. How will you calculate the number of particles N_n in a system with energy ϵ_n ? What is the total number of particles if the system is discrete?
21. Write down an expression for the total number of energy states in the interval $d\epsilon$ and explain the symbols.
22. What does MB statistics deal with?
23. What does BE statistics deal with?

24. What does FD statistics deal with?
25. Write down Maxwell-Boltzmann energy distribution law and explain the symbols.
26. Write down Maxwell-Boltzmann speed distribution law and explain the symbols.
27. Write down the mathematical condition to be satisfied for treating particle as classical.
28. What are bosons? Give three examples.
29. What are the properties of bosons?
30. What are fermions? Give three examples.
31. What are the properties of fermions.
32. Distinguish between fermions and bosons.
33. Write down the Bose-Einstein distribution law and explain the symbols.
34. What is a photon gas?
35. Write down the Planck's radiation law and explain the symbols.
36. Classify the following particles according to BE and FD statistics. Proton, neutron, electron, photon, α particle, hydrogen atom, hydrogen molecule, positron and lithium ion ${}^6_3\text{Li}^+$
37. Write down Fermi-Dirac energy distribution law for free electrons in a metal and explain the symbols.
38. Define Fermi energy.
39. For $T > 0\text{K}$ and $\varepsilon = \varepsilon_F$, show that probability is only 50%.
40. Write down three applications of FD statistics.

Section B

(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type questions

1. Briefly explain the statistical analysis of a composite system.
2. Distinguish between classical and quantum statistical mechanics.
3. Show that the most probable energy in the case of Maxwell-Boltzmann distribution is $\frac{1}{2}kT$.
4. Derive an expression for v_{rms} starting from Maxwell-Boltzmann speed distribution law.
5. Derive an expression for average speed starting from Maxwell-Boltzmann speed distribution law.
6. Derive an expression for most probable speed starting from Maxwell-Boltzmann speed distribution law.
7. Explain the experimental determination of molecular speeds.
8. Derive an expression for Fermi energy.
9. Derive an expression for average Fermi energy.

10. Derive the condition for the limits of classical statistics.
11. Derive Planck's radiation law by assuming Bose-Einstein distribution law and density of states.
12. Arrive at Stefan's law using Bose-Einstein distribution law.
13. a) Considering the numbers of heads and tails, how many macrostates are there when 5 coins are tossed
 b) What is the total number of possible microstates in tossing 5 coins
 c) Find the number of microstates for each macrostate.
 [a) 6 b) 32 c) 1, 5, 10, 10, 5, 1]
14. Consider a system consisting of two particles, one with spin $s = 1$ and another with spin $s = \frac{1}{2}$. a) Considering a microstate to be an assignment of the z-component of the spins of each of the particles what is the total number of microstates of the two particle system. b) How many macrostates are there for the total spin at the two particle system. c) Find the number of states of each macrostate. [a) 6 b) 2 c) 4, 2]
15. A system containing 10 electrons. Calculate the total number of microstates possible
 [2^{10}]
16. A system consists of two particles each of which has a spin of $\frac{3}{2}$. a) Assuming the particles to be distinguishable, what are the macrostates of the total spin and what is the multiplicity of each. b) What are the possible values of total spin and what is the multiplicity of each value. c) Suppose the particles behave like indistinguishable quantum particles. What is the multiplicity of the macrostates of the total spin?
 [a) 7, 16 b) 7, 5, 3, 1 c) 10]
17. In a conductor like copper, each atom provides one electron that is available to conduct electric currents. If we assume that the electrons behave like a gas of particles at room temperature with a most probable energy of 0.0252 eV. What is the density of states in interval of 1% about the most probable energy.
 [$\approx 2.7 \times 10^{23} \text{ m}^{-3}$]
18. A system consists of N particles that can occupy two energy levels a non-degenerate ground state and a 3 fold degenerate excited state which is at an energy of 0.25 eV above the ground state. At a temperature of 960 K, Find the number of particles in the ground state and in the excited state.

$$\begin{cases} N_1 = 0.872 N \\ N_2 = 0.128 N \end{cases}$$
19. A container holds one mole of helium gas at a temperature of 293 K. Calculate the mean energy of the molecules. How many molecules have energies in an interval of 0.01 times mean energy centred on mean energy?

$$\begin{cases} 0.0379 \\ 3.46 \times 10^{21} \end{cases}$$

20. Check whether the Maxwell-Boltzmann statistics can be applied to the following
 a) liquid helium at 4K b) conduction electrons in copper at room temperature.

[a) yes b) no]

21. What pressure must be applied to nitrogen gas at room temperature before Maxwell-Boltzmann statistics begins to fail? [P = 10³ atm]

22. To what temperature we must cool nitrogen gas at 1 atmospheric pressure before M.B. statistics fail. [= 2.9K]

23. Calculate the number of photons per cm³ in a volume filled with radiation at 3K.

$$\text{Given } \int_0^{\infty} \frac{x^2 dx}{e^x - 1} = 2.404 \quad [540 \text{ photons/cm}^3.]$$

24. The human eye is most sensitive to that wavelength (λ_{\max}) at which energy distribution of solar radiation shows the maximum. Calculate λ_{\max} if surface temperature is 5730K. [5.058 × 10⁻⁷ m]

25. Show that the total number of photons per unit volume of an enclosure at temperature

$$T \text{ is } 16 \left(\frac{kT}{hc} \right)^3 \sum_{n=1}^{\infty} \frac{1}{n^3} \text{ starting from Planck's radiation law.}$$

26. An object is at a temperature of 400°C. At what temperature would it radiate energy twice as fast. [527.34°C]

27. A metal sphere 4cm in diameter whose emissivity is 0.25 is heated in a furnace to 500°C. At what rate does it radiate. [25.42W]

28. Find the surface area of a black body that radiates 1kW when temperature is 500°C. If the black body is a sphere, what is its radius. [6.27cm]

29. The brightest part of the spectrum of the star sirius is located at a wavelength of about 290nm. What is the surface temperature of the star. [10⁴K]

30. The microprocessors used in computers produce heat at rates as high as 30W per cm² of surface area. At what temperature would a black body be if it had such a radiance. [1517K]

31. The density of aluminium is 2.7 gcm⁻³ and its atomic mass is 26.97g/mole. The effective mass of an electron in aluminium is 0.09m_e. Calculate Fermi energy in aluminium. [11.8eV]

32. The Fermi energy in silver is 5.51eV. (a) What is the average energy of the free electrons in silver at 0K. b) What temperature is necessary for the average molecular energy in an ideal gas to have this value. [3.31eV, 3.84 × 10⁴K]

33. Using F.D. distribution function for electrons show that in a system of electron gas at $T = 0$ all states of $\epsilon > \epsilon_F$ are unoccupied.
34. The number of conduction electrons per cm^3 is 24.2×10^{22} in beryllium and 0.91×10^{22} in cesium. If the Fermi energy of conduction electrons in Be is 14.44eV . Calculate that in cesium. [1.587eV]

Section C

(Answer questions in about two pages)

Long answer type questions (Essays)

- Derive an expression for density of states of particles in a gas.
- Derive Planck's radiation law using B.E. statistical distribution law. Also deduce Wein's displacement law from it.
- What is F-D statistics? Derive an expression for Fermi-Dirac distribution law of electrons.

Hints to problems

1 to 12 See book work

13. a)	H	T	$W = \frac{N!}{n_1!n_2!}$
	5	0	1
	4	1	5
	3	2	10
	2	3	10
	1	4	5
	0	5	1

Total number of macrostates = 6

Total number of microstates = $2^5 = 32$

14. a) For $s = 1$, there are $(2s + 1)$ microstates = 3

For $s = \frac{1}{2}$, there are $(2s + 1)$ microstates = 2

∴ Total number of microstates = $3 \times 2 = 6$.

- b) Two spins can combine to give either $1 + \frac{1}{2} = \frac{3}{2}$ or $1 - \frac{1}{2} = \frac{1}{2}$. So there are two macrostates.

- c) For $s = \frac{3}{2}$ there are $(2 \times \frac{3}{2} + 1) = 4$ microstates and $s = \frac{1}{2}$, there are $(2 \times \frac{1}{2} + 1) = 2$ microstates

- \therefore Total $4 + 2$ microstates.
15. Each electron has $(2s + 1)$ states
 \therefore The number of microstates possible is $(2s + 1)^{10} = 2^{10}$.
16. a) Each particle has $2s + 1 = 2 \times \frac{3}{2} + 1 = 4$ states.
 \therefore The total number of macrostates $= 4 \times 4 = 16$
- For each particle the possible states are

$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$ and $-\frac{3}{2}$
and $\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$ and $-\frac{3}{2}$

The total spin of the system $s = 3$

The possible states $+3, 2, 1, 0, -1, -2$ and -3 .

7 Macrostates	Multiplicity
3 $(\frac{3}{2}, \frac{3}{2})$	1
2 $(\frac{3}{2}, \frac{1}{2}) (\frac{1}{2}, \frac{3}{2})$	2
1 $(\frac{3}{2}, -\frac{1}{2}) (\frac{1}{2}, \frac{1}{2}) (-\frac{1}{2}, \frac{3}{2})$	3
0 $(\frac{3}{2}, -\frac{3}{2}) (-\frac{3}{2}, \frac{3}{2}) (\frac{1}{2}, -\frac{1}{2}) (-\frac{1}{2}, \frac{1}{2})$	4
-1 $(-\frac{3}{2}, \frac{1}{2}) (\frac{1}{2}, -\frac{3}{2}) (-\frac{1}{2}, -\frac{1}{2})$	3
-2 $(-\frac{3}{2}, -\frac{1}{2}) (-\frac{1}{2}, -\frac{3}{2})$	2
-3 $(-\frac{3}{2}, -\frac{3}{2})$	1
<hr/> <hr/> Total 16	

- b) The possible values of total spin are $s = 3, 2, 1, 0$
For $s = 3$, the multiplicity $= 2s + 1 = 2 \times 3 + 1 = 7$
For $s = 2$, the multiplicity $= 2s + 1 = 2 \times 2 + 1 = 5$
For $s = 1$, the multiplicity $= 2s + 1 = 2 \times 1 + 1 = 3$
For $s = 0$, the multiplicity $= 2s + 1 = 2 \times 0 + 1 = 1$
Total multiplicity $= 7 + 5 + 3 + 1 = 16$.
- c) When the particles are indistinguishable look at the table drawn for (a)

	Multiplicity
3 $(\frac{3}{2}, \frac{3}{2})$	1
2 $(\frac{3}{2}, \frac{1}{2})$	1
1 $(\frac{3}{2}, -\frac{1}{2}) (\frac{1}{2}, \frac{1}{2})$	2
0 $(\frac{3}{2}, -\frac{3}{2}) (\frac{1}{2}, -\frac{1}{2})$	2
-1 $(-\frac{3}{2}, -\frac{1}{2}) (-\frac{1}{2}, -\frac{1}{2})$	2
-2 $(-\frac{3}{2}, -\frac{1}{2})$	1
-3 $(-\frac{3}{2}, -\frac{3}{2})$	1
	<u>Total 10</u>

17. Using $g(\epsilon)d\epsilon = \frac{8\pi\sqrt{2}m^{3/2}\epsilon^{1/2}}{h^3}d\epsilon$

$$m = 9.1 \times 10^{-31}, \quad \epsilon = 0.0252 \text{ eV}, \quad d\epsilon = 0.0252 \times \frac{1}{100} \text{ and } h = 6.64 \times 10^{-34}$$

18. $N \propto de^{-\frac{\epsilon}{kT}}$ ∴ $\frac{N_2}{N_1} = \frac{d_2 e^{-\frac{\epsilon_2}{kT}}}{d_1 e^{-\frac{\epsilon_1}{kT}}} = \frac{3}{1} e^{-\frac{(\epsilon_2 - \epsilon_1)}{kT}}$

$$\epsilon_2 - \epsilon_1 = 0.25 \text{ eV}$$

$$kT = 8.625 \times 10^{-5} \times 960 = 9.28 \times 10^{-2}$$

$$\frac{N_2}{N_1} = 3e^{-\frac{0.25}{9.28 \times 10^{-2}}} = 3e^{-3.019} = 0.147$$

$$N_1 + N_2 = N \quad \therefore \quad N_2 = N - N_1$$

$$\therefore \frac{N - N_1}{N_1} = 0.147 \quad \therefore N_1 = 0.872N \quad \text{and} \quad N_2 = 0.128N$$

19. Mean energy, $E_m = \frac{3}{2}kT = \frac{3}{2} \times 8.625 \times 10^{-5} \times 293$
 $= 0.0379 \text{ eV}$

$$\begin{aligned} dN = N(\varepsilon)d\varepsilon &= \frac{2N}{\sqrt{\pi(kT)^{3/2}}} \varepsilon_m^{1/2} e^{-\frac{\varepsilon_m}{kT}} d\varepsilon \\ &= \frac{2 \times 6.02 \times 10^{23} \times (0.0379)^{1/2}}{\sqrt{3.14}(0.02527)^{3/2}} e^{-\frac{0.0379}{0.02527}} \times 0.01 \times 0.0379 \\ &= 3.46 \times 10^{21} \end{aligned}$$

20. See example 13.

21. M.B statistics fail when $\frac{\lambda}{d}$ is less than (say 0.1) but not very much less than 1.

$$\lambda = \frac{h}{\sqrt{2mkT}}, \quad d = \left(\frac{V}{N}\right)^{1/3}$$

$$\text{Using } PV = NkT \quad \frac{V}{N} = \frac{kT}{P}$$

$$\text{Then calculate } P, \text{ substituting, we get } P = \frac{0.1(2m)^{3/2}(kT)^{3/2}}{h^3}$$

$$m_{N_2} = 28u = 28 \times 1.67 \times 10^{-27} \text{ kg}$$

22. For the validity of M.B statistics $\frac{h}{\sqrt{2mkT}} \left(\frac{N}{V}\right)^{1/3} \ll 1$, Begins to fail

$$\frac{h}{\sqrt{2mkT}} \left(\frac{N}{V}\right)^{2/3} = 0.1$$

$$\text{Use } \frac{N}{V} = \frac{P}{kT} \text{ Find } T$$

23. See example 1

$$24. \lambda_{\max} T = 2.898 \times 10^{-3}$$

25. See book work.

26. Energy radiated, $E \propto T^4$

$$\therefore \frac{E_2}{E_1} = \left(\frac{T_2}{T_1} \right)^4 \quad E_2 = 2E_1 \quad \text{given} \quad T_1 = 400 + 273 = 673\text{K.}$$

27. Energy radiated per second per unit area = $e \sigma T^4$

$$\therefore \text{Energy radiated per second} = 4\pi r^2 e \sigma T^4 \\ = 4 \times 3.14 \times (2 \times 10^{-2})^2 \times 0.25 \times 5.67 \times 10^{-8} \times (773)^4$$

28. Energy radiated per second = $4\pi r^2 \sigma T^4$

$$10^3 = 4\pi r^2 \sigma T^4 \quad \text{or} \quad r^2 = \frac{10^3}{4\pi \times \sigma T^4} \quad r = \left(\frac{10^3}{4\pi e \sigma T^4} \right)^{\frac{1}{2}}$$

$$\sigma = 5.67 \times 10^{-8}, \quad T = 773\text{K}$$

$$29. \lambda_{\max} T = 2.898 \times 10^{-3} \quad T = \frac{2.898}{290 \times 10^{-9}} \times 10^{-3} \approx 1 \times 10^4 \text{ K.}$$

$$30. R = \sigma T^4 \quad T = \left(\frac{R}{\sigma} \right)^{\frac{1}{4}} = \left(\frac{30 \times 10^4}{5.67 \times 10^{-8}} \right)^{\frac{1}{4}}$$

31. Same as example 20

$$32. \text{a) } \bar{\varepsilon}_0 = \frac{3}{5} \varepsilon_F \quad \text{b) } 3.31\text{eV} \approx kT \quad T = \frac{3.31 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}}$$

33. See book work

$$34. E_F \propto \left(\frac{N}{V} \right)^{\frac{2}{3}}$$

$$(E_F)_{Cs} \propto (0.9 \times 10^{22})^{\frac{2}{3}} \quad \dots \dots (1)$$

$$(E_F)_{Be} \propto (24.2 \times 10^{22})^{\frac{2}{3}} \quad \dots \dots (2)$$

$$(E_F)_{Be} = 14.44\text{eV}$$

$\frac{\text{eqn 1}}{\text{eqn 2}}$ gives the answer.
